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A QUARTERLY SUPPLEMENT
of the
PHILOSOPHICAL MAGAZINE

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VOLUME 10 OCTOBER 1961 NUMBER 40

PRICE per part **25*s*.** plus postage
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A History of Mathematics

From antiquity to the early nineteenth century

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Methods of Measuring Debye Temperatures and Comparison of Results for some Cubic Crystals

By F. H. HERBSTEIN

National Physical Research Laboratory, Council for Scientific and Industrial Research, Pretoria, South Africa

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§ 1. INTRODUCTION

THE frequency spectrum of the coupled vibrations of the atoms in a crystal lattice has fascinated theoretical physicists since before the beginning of the century because of its intrinsic interest as a mathematical problem, and its importance in many branches of solid-state physics. Despite considerable effort, a mathematically exact calculation of the frequency spectrum has not yet been achieved although a number of semi-empirical calculations, with varying degrees of approximation, have been made (Blackman 1955 a for summary). The frequency spectra of a few elements have been determined experimentally by applying Born's (1942–3) theory to the measured diffuse scattering of x-rays from Cu (Jacobsen 1955), α–Fe (Curien 1952) and Al (Walker 1956 a). Similar determinations have been made for V by using the incoherent inelastic scattering of cold neutrons (Stewart and Brockhouse 1958, Eisenhauer *et al.* 1958) and for Al by using the coherent inelastic scattering of cold neutrons (Carter *et al.* 1957, Brockhouse and Stewart 1958). Actual frequency spectra are so complex that approximate forms are still of considerable practical importance in calculating such quantities as specific heats, atomic vibration amplitudes in crystals, x-ray temperature factors and temperature diffuse scattering in elements and alloys and also for estimating thermal entropies. An important new application is to the study of the recoilless emission and absorption of nuclear gamma radiation in solids (the Mössbauer effect).

The most widely used approximate frequency spectrum is the parabolic distribution first introduced by Debye (1912) and since known by his name. This frequency spectrum is usually described in terms of the characteristic or Debye temperature† which is related to the maximum vibration frequency of the lattice ν_m by $\Theta = h\nu_m/k$ (h Planck's constant, k Boltzmann's constant).

Current interest in Debye temperatures is in two directions. Firstly there is the desire to test the theoretical prediction that different methods of measuring Debye temperatures will give the same numerical values at temperatures approaching absolute zero. Experimental results obtained in the last few years confirm the theory (Alers and Neighbours 1959, § 7.1). Secondly there is the need to use Debye temperatures (now referring to arbitrary temperatures of interest) to calculate many physical parameters of solids. There are a number of different methods of determining the Debye temperature of a solid; these depend differently on the deviation of the true frequency spectrum from its assumed parabolic form and also differ greatly in convenience and ease of application. It is therefore important to determine whether the values of Θ obtained from various experiments can be used interchangeably and whether the differences among the experimental values agree with theoretical predictions. In this paper the assumptions on which the Debye theory are based are first reviewed and the different experimental methods are then discussed. Values of Debye temperatures, determined by different techniques at 0°K, at room temperature and over a range of temperatures, have been taken from the literature for nineteen different cubic elements and these are critically compared. A brief account of the principal results has been presented (Herbstein 1960).

---

† In this paper the Debye temperature is denoted by Θ when reference to a particular experimental method is not intended. Debye temperatures determined by the various experimental methods are differentiated by subscripts: thus Θ_D refers to specific heat measurements, Θ_M to diffraction methods, and Θ_R to resistivity measurements.

There have been a number of excellent reviews published recently dealing with various aspects of the vibrational spectra of crystals. One of the most comprehensive of these is the article by Blackman (1955 a) in *Handbuch der Physik*, which covers both the Debye and Born–von Karman theories of specific heats and includes a detailed bibliography which will not be duplicated here. De Launay's (1956) review covers similar ground, while Cole (1959) has presented a short and not too technical introduction to the subject, with emphasis on the use of diffraction methods for deriving the frequency spectrum. An excellent account of the effects of lattice vibrations on x-ray diffraction patterns of crystals has been given by James (1950), while more detailed treatments are due to Laval (1958) and to Slater (1958) who has reviewed the general theoretical background.

§ 2. Assumptions of the Debye Approximation

In the Debye approximation it is assumed that the crystal lattice can be treated as an isotropic elastic continuum. It follows that the frequency distribution function is

$$\begin{aligned} N(\nu)\,d\nu &= 4\pi\left(\frac{1}{C_l^3}+\frac{2}{C_t^3}\right)V\nu^2\,d\nu \qquad \nu\leqslant\nu_m \\ &= 0 \qquad\qquad\qquad\qquad\qquad\qquad \nu>\nu_m \end{aligned}$$

where $N(\nu)$ is the number of frequencies between ν and $\nu+d\nu$, C_l and C_t are the velocities of the longitudinal and transverse elastic waves respectively and V is the volume of the crystal. It was assumed that C_l and C_t are invariant with respect to direction in the crystal and wavelength of the elastic wave (i.e. there is no dispersion). The atomic structure of crystals was then taken into account in the theory of specific heats by setting the same lower limit to the wavelengths of the longitudinal and transverse waves. Consequently there will be different upper limits to the frequency distributions of the transverse and longitudinal waves and an avarage maximum frequency ν_m must be chosen. This must be such that the number of normal vibrations is $3N$, where N is the number of atoms in the crystal. Thus

$$\int_0^{\nu_m} a\nu^2\,d\nu=3N \quad \text{or} \quad \nu_m=(9N/a)^{1/3} \qquad . \quad . \quad . \quad . \quad (1)$$

where $a=4\pi V(C_l^{-3}+2C_t^{-3})$.

As mentioned above the Debye temperature is then defined in terms of the cut-off frequency by $\Theta=h\nu_m/k$. As the method of averaging the maximum frequencies for the different vibrational modes is not the same in specific-heat theory as in the theory of the x-ray temperature factor, the respective Debye temperatures will differ slightly. This is discussed in more detail in § 4.

The basic assumptions of the Debye approximation—simple harmonic vibrations, elastic isotropy, no dispersion—are by no means fully realized in practice and thus lead to restrictions on the applicability of the theory. Anharmonicity of atomic vibrations and the existence of dispersion appear to affect only the details of the vibration spectrum, but the condition of elastic isotropy suggests that it is best to restrict application of the Debye theory to cubic crystals (even among cubic crystals only W, and to a lesser extent Al, are approximately elastically isotropic). Elastic anisotropy is compensated for semi-empirically to a considerable extent as the frequency spectrum is in fact an average taken all over all directions in the crystal lattice. A further restriction is to crystals with only one atom in the primitive unit cell; this is because only the acoustic branch of the spectrum is included. The setting of a lower bound to the elastic wavelength in the lattice, independent of direction, involves the approximation of replacing the first Brillouin zone of the crystal by a sphere. This holds fairly accurately for body-centred and face-centred cubic crystals but less well for simple cubic crystals (Slater 1939).

Reliable vibrational spectra have been determined for a number of elements (e.g. Al, Cu, V) and these are very different from the corresponding parabolic forms and, indeed, appreciably different from the spectra calculated by lattice dynamics on the basis of various simplifying approximations. Despite the lack of realism in the basic assumptions of the Debye approximation, and the resultant differences between the true vibrational spectra and the parabolic approximation, the effects are not very severe for such properties as specific heat, vibrational entropy and x-ray temperature factor where integration over the whole frequency spectrum is required. This is a natural consequence of the averaging process implicit in the integration. A further compensating factor is provided by the semi-empirical nature of the Debye approximation because the parabolic frequency distribution, and hence Θ, is chosen to give the best fit between theory and the particular experimental result obtained. On the basis of these arguments, the Debye approximation would be expected to be much more successful in practice than the inappropriateness of its initial assumptions might lead one to suppose. This is borne out both by past experience and by the results summarized here.

§ 3. EXPERIMENTAL METHODS FOR DETERMINING DEBYE TEMPERATURES

3.1. *Specific Heat Measurements*

The classical method of determining the Debye temperature is from measurement of the specific heat. It is necessary to subtract the electronic specific heat from the measured values and to convert the measured C_p to C_V using the thermodynamic equation $C_p - C_V = \beta^2 VT/\chi$ where β is the coefficient of volume expansion and χ the isothermal compressibility. Debye's equation for the heat capacity of 1 g-atom of solid is

$$C_V = 9Nk\frac{T^3}{\Theta_D{}^3}\int_0^x \frac{p^4 e^p}{(e^p-1)^2}\,dp. \qquad (2)$$

where N is Avogadro's number, k Boltzman's constant,

$$x = \frac{\Theta_D}{T} \quad \text{and} \quad \Theta_D = \frac{h\nu_D}{k}.$$

The usual procedure is to calculate Θ_D from eqn. (2) using measured values of C_V. Plots of Θ_D against T show that Θ_D is not constant as it would be if Debye's assumptions were valid. The variations of Θ_D with T can be explained in terms of the Born–von Karman theory of lattice vibrations. For purposes of comparison with the results of other experimental methods, the variation of Θ_D with T makes a choice of Θ_D difficult. Blackman (1955 a, table 9, p. 364) has used $T = \frac{1}{2}\Theta_D$ as a convenient standard temperature as "This temperature is sufficiently high to give fair agreement over most of the specific heat curve, and sufficiently low for errors in the $(C_P - C_V)$ correction to be small". The correction for the electronic specific heat will also be negligible at this temperature. Blackman's usage has been followed in selecting the Θ_D values given later in the tables, where they are nominally referred to a temperature of 300°K. Recent measurements of Θ_D for many elements over a range of temperatures have been summarized by De Sorbo (1954) while Θ_D values determined at very low temperatures have been given by Alers and Neighbours (1959).

3.2. *Entropy Measurements*

Θ_D values can be derived from calorimetric entropy measurements using the equation (Lumsden 1952):

$$S = R\left(4 - 3\ln x + \frac{3x^2}{40} - \frac{3x^4}{2240} - \frac{x^6}{36288} - \frac{x^8}{1\,689\,600} + \dots\right) \tag{3}$$

where $x = \Theta_D/T$. Lumsden has also reported values for a number of metals which are included in the tables of experimental results. The measured entropy values used in (3) must, of course, be corrected for electronic and other non-vibrational contributions. One use of eqn. (3) is for the calculation of vibrational contributions to the entropy of alloys, using Debye temperatures measured in other experiments.

3.3. *Measurements of Elastic Constants*

3.3.1. *Polycrystalline samples*

Polycrystalline samples of small grain size are effectively isotropic if free from preferred orientation so that Debye's original derivation (1912) of Θ from the elastic constants of an isotropic continuum applies. Different expressions are obtained for Θ_M and Θ_D, the Debye temperatures appropriate to diffraction and specific-heat measurements respectively, because different methods of averaging over the longitudinal and transverse vibrations are used (see § 4). It is convenient to express these values in terms of Young's modulus (E) rather than the bulk modulus (K) originally used by Debye because the equations then depend on functions of Poisson's ratio (σ) which vary very slowly in the region of interest. The equations given below were derived from those given by Debye (cf. James (1950)) by making the substitution $K = E/3(1-2\sigma)$ *before* averaging over the longitudinal and transverse values of Θ. We obtain

$$\Theta_{\mathrm{M}} = \frac{h\sqrt{3}}{k}\left(\frac{3N}{4\pi}\right)^{1/3}\frac{E^{1/2}}{m^{1/3}\rho^{1/6}}\, f_1(\sigma) \quad . \; . \; . \; . \; . \; . \quad (4)$$

with

$$f_1(\sigma) = \left[\frac{3-5\sigma}{(15-26\sigma)(1+\sigma)}\right]^{1/2}, \quad . \; . \; . \; . \; . \; . \quad (4a)$$

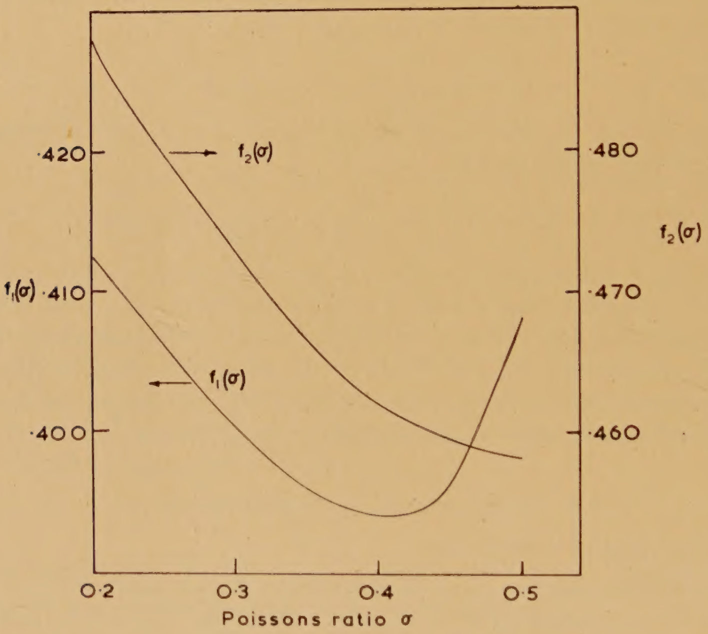
$$\Theta_{\mathrm{D}} = \frac{h}{k}\left(\frac{9N}{4\pi}\right)^{1/3}\frac{E^{1/2}}{m^{1/3}\rho^{1/6}}\, f_2(\sigma), \quad . \; . \; . \; . \; . \; . \quad (5)$$

with

$$f_2(\sigma) = \left(\frac{3-5\sigma}{1+\sigma}\right)^{1/2}\{2^{5/2}(3-5\sigma) + 3^{3/2}(1-2\sigma)\}. \quad . \; . \; . \; . \quad (5a)$$

In these equations m is the atomic weight (for an alloy the mean atomic weight should be taken), ρ is the density and N is Avogadro's number. $f_1(\sigma)$ and $f_2(\sigma)$ are insensitive functions of σ in the range $0{\cdot}2 < \sigma < 0{\cdot}5$ (see fig. 1) in which all the values for metals cited by Koster (1954) lie. Consequently simpler approximate forms of (4) and (5) can be given; for example $\Theta_{\mathrm{M}} \approx 12\,(Ea/A)^{1/2}$ for face-centred cubic materials, where E is in kg/mm^2, A is in atomic units (i.e. $^{12}\mathrm{C} = 12$) and a is the lattice parameter in angstroms.

Fig. 1



Variation of $f_1(\sigma)$ (eqn. (4 a)) and $f_2(\sigma)$ (eqn. (5 a)) with σ (Poisson's ratio).

Values of the elastic constants can be measured either by static or dynamic methods. Useful summaries of measured values of elastic constants for polycrystalline metals and alloys have been given by Koster (1948 a, b, 1954).

3.3.2. *Single-crystal samples*

The Debye temperature can be expressed as

$$\Theta_{\mathrm{D}}=\frac{h}{k}\left(\frac{3}{4\pi V_{\mathrm{a}}}\right)\langle C\rangle$$

where V_{a} is the volume per atom and $\langle C\rangle$ is the mean velocity of the elastic waves in the lattice and is defined by

$$3\langle C\rangle^{-3}=\sum_{i} C_i^{-3}, \quad i=1,\ 2,\ 3$$

in which the C_i are the three velocities of propagation of plane elastic waves in the crystal, averaged over all directions in the lattice. A fairly large number of methods of calculating $\langle C\rangle$ from the measured elastic constants have been devised and are summarized by Blackman (1955 a). The present calculations of Θ_{D} from measured c_{ij} values were made using the method† of Quimby and Sutton (1953) and Sutton (1955).

Elastic constants are usually measured by ultrasonic pulse-velocity methods and comprehensive reviews of theory and results have been given by Hearmon (1946) and Huntingdon (1958).

3.4. *Diffraction Measurements*

Much of the subject matter of this section is discussed in detail by James (1950, chapter V) where derivations of many of the equations used here will be found.

3.4.1. *Measurement of Bragg intensities at a given temperature*

For a monatomic cubic lattice the structure factor of the Bragg reflection *hkl* is given by

$$K F^2(hkl)=f^2(hkl)\exp(-2M). \qquad \ldots \ldots \quad (6)$$

Equation (6) is applicable to diffraction measurements in general if $f(hkl)$ is understood to denote the atomic scattering factor $f_x(hkl)$ for x-ray diffraction, the atomic potential factor

$$g(hkl)=\frac{e}{4\pi}\left(\frac{Z-f_x(hkl)}{(\sin\theta/\lambda)^2}\right)$$

for electron diffraction or the nuclear scattering length b for neutron diffraction. $F(hkl)$ is the structure factor derived from the corresponding measured intensity by standard methods in each case. $2M=2B(\sin^2\theta/\lambda^2)$ is the Debye–Waller temperature factor, θ is the Bragg angle, λ is the wavelength of the radiation used and K is a normalizing factor depending both on the experimental arrangement and the symmetry of the lattice. An accurate experimental value of K can be obtained relatively easily for neutron diffraction (Bacon 1955, p. 93) but this is much more difficult for x-ray or electron diffraction.

---

† The calculations were done on the Stantec Zebra electronic computer in our laboratory, using a programme prepared by Miss S. A. Gous.

From (6) it follows that

$$\ln\left(\frac{f^2}{F^2}\right)=\ln K+2B\frac{\sin^2\theta}{\lambda^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus a plot of $\ln(f^2/F^2)$ against $\sin^2\theta/\lambda^2$ will give both B, from the slope of the plot and $\ln K$, from the intercept at $\sin^2\theta/\lambda^2=0$. The value of Θ_M is obtained from the measured value of B by using the Debye–Waller formula (Debye 1914, Waller 1923)

$$2B=\frac{12h^2T\psi(x)}{mk\Theta_M{}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where m is the mass of the atom, T is the absolute temperature of the sample, $x=\Theta_M/T$ and

$$\psi(x)=\frac{1}{x}\int_0^x\frac{u\,du}{e^u-1}+\frac{x}{4}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$\psi(x)$ varies from 1·000 to 1·164 for $0\leqslant x\leqslant 2{\cdot}5$ and thus (8) can be solved for Θ_M by a series of successive approximations.

The great majority of values of Θ_M derived from diffraction measurements have been obtained by x-ray diffraction. Intensity measurements in electron diffraction are complicated by theoretical and experimental difficulties so that this method has been little used. Only one independent value of Θ_M has so far been derived from neutron-diffraction intensity measurements (Henshaw 1958) but this method does have one definite advantage over others which is discussed below.

There are a number of problems involved in the use of eqn. (6) which must be mentioned. The first of these is the necessity of correcting Bragg intensity measurements for a contribution from the temperature-diffuse scattering (TDS). The form of this correction, which must be applied to intensity measurements in all types of diffraction experiments, has only been published recently (Nilsson (1957), Chipman and Paskin (1959 b)). In x-ray diffraction measurements, for example, the Bragg peaks are superimposed on a background of Compton scattering and temperature-diffuse scattering. The former is a smooth function in diffraction space but the latter has maxima at the same positions as the Bragg reflections. Thus the true intensity of the Bragg reflection must be obtained by subtracting the calculated TDS peak area from the measured total peak area, taking both over the same angular range. The importance of this correction varies with the material investigated; for single-crystal measurements on NaCl, Nilsson estimates that application of the correction reduces Renninger's (1952) measured Θ_M from 319°K to 302°K.

There is a further difficulty which applies to x-ray and electron diffraction but not to neutron diffraction. This is that the atomic scattering factors are themselves theoretical quantities calculated from necessarily imperfectly known electron distributions in atoms; in x-ray diffraction it is further necessary to correct the tabulated values for anomalous dispersion (James 1950, chapter IV, Parratt and Hempstead 1954, Dauben and Templeton 1955) and this correction is sometimes difficult to apply accurately. Neutron diffraction has the great advantage that the nuclear scattering length does not vary with scattering angle. Although the nuclear scattering lengths are empirical quantities, accurate values are available for most elements (Bacon 1955).

Borie (1956) has proposed a method of determining both the atomic scattering factor and the Debye temperature from the x-ray powder pattern of an element. This method requires measurements of the integrated intensities of the Bragg peaks and the intensity of the diffuse background, using monochromatic radiation. The temperature diffuse contribution to the background is obtained by subtracting the calculated Compton scattering from the measured values. The TDS (for a powder pattern) can be written as

$$I_{\mathrm{TDS}}\left(\frac{\sin\theta}{\lambda}\right)=f^2(1-\exp(-2M))\,G\left(\frac{\sin\theta}{\lambda}\right) \quad . \quad . \quad . \quad (10)$$

where $G(\sin\theta/\lambda)$ is a radial function in reciprocal space whose form has been given by Warren (1953), Herbstein and Averbach (1955) and Paskin (1959)† for a variety of situations. Thus $f^2[1-\exp(-2M)]$ can be obtained as a function of $(\sin\theta/\lambda)$ from the TDS while the Bragg intensities give $f^2\exp(-2M)$ as a function of $(\sin\theta/\lambda)$. The sum of the two curves is f^2 and their ratio is $[\exp(2M)-1]$. This method has been applied with reasonable success to copper. One difficulty is the calculation of the Compton scattering, which amounts to about 30% of the background for copper, and which is known with an accuracy of about 10%. Chipman (1960) has estimated that the resultant uncertainty in Θ_{M} of copper is ±10°K.

3.4.2. *Comparison of Bragg-intensity measurements at different temperatures*

Measurements at different temperatures can be used as follows:

$$\text{at}\quad T_1: F_1(hkl)=Kf\left(\frac{\sin\theta}{\lambda}\right)_1\exp\left[-B_1\left(\frac{\sin^2\theta}{\lambda^2}\right)_1\right],$$

$$\text{at}\quad T_2: F_2(hkl)=Kf\left(\frac{\sin\theta}{\lambda}\right)_2\exp\left[-B_2\left(\frac{\sin^2\theta}{\lambda^2}\right)_2\right].$$

(It is assumed that any changes in Bragg angle due to thermal expansion have been allowed for in the derivation of structure factors from measured intensities.) If (7) and (8) are now used, Θ_{M} being treated as varying with temperature, we obtain

$$\ln\left[\frac{gF_1}{F_2}\right]=\left\{\frac{B_2}{4a_2^{\,2}}-\frac{B_1}{4a_1^{\,2}}\right\}(h^2+k^2+l^2)$$

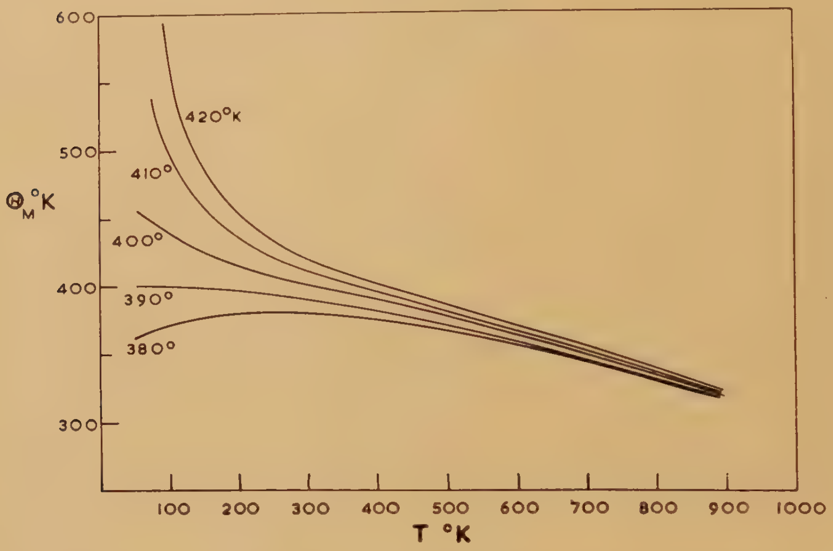
$$=\frac{3h^2}{2mk}\left\{\frac{T_2\psi(x_2)}{a_2^{\,2}\,\Theta_{\mathrm{M}2}^{\,2}}-\frac{T_1\psi(x_1)}{a_1^{\,2}\,\Theta_{\mathrm{M}1}^{\,2}}\right\}(h^2+k^2+l^2) \quad . \quad . \quad . \quad (11)$$

---

† See note added in proof.

where $\psi(x)$ is defined in eqn. (9). g is a correction factor, differing only slightly from unity, which allows for the change of atomic scattering factor with angle in x-ray and electron diffraction. For neutron diffraction $g \equiv 1$. Thus the slope of the plot of $\ln(gF_1/F_2)$ against $(h^2+k^2+l^2)$ will give an equation relating Θ_{M1} and Θ_{M2}; this can be solved directly if Θ_{M1} is known from a separate experiment. Alternatively it has often been assumed that it is permissible to take Θ_M as constant over small temperature intervals. The smaller the temperature interval the better this assumption, but also the smaller the difference in F_1 and F_2: clearly very accurate intensity measurements are necessary for this method to work well.

Fig. 2



Θ_M of aluminium versus temperature obtained from experimental intensity measurements. The various curves were obtained by choosing Θ_M at 300°K equal to 380°, 390°, 400°, 410° and 420°K respectively. This figure taken from Chipman (1960).

When measurements are made at a number of temperatures it is usual to compute all the results with reference to a standard temperature T_1, usually room temperature, and then plot $(h^2+k^2+l^2)^{-1}\ln(gF_1/F_2)$ against T_2. Some workers have then proceeded by assuming a particular form for the temperature-dependence of Θ_M, such as that given by assuming that the temperature-dependence of Θ_M is due to thermal expansion only (see § 5). This procedure fails when its basic assumption is violated, as has been demonstrated for silver (Herbstein 1961). A more objective method of analysing the results has been proposed by Chipman (1960) who pointed out that the dependence of Θ_M on T is itself dependent on the value chosen for Θ_{M1}. This is illustrated in fig. 2. The latitude introduced in this way is limited by the fact that only certain forms of the curve of Θ_M against T are physically reasonable. Choice of the appropriate value of Θ_{M1} is complicated by the fact that these curves differ significantly in shape only at fairly low temperatures, and thus experimental data below $T \sim \Theta_M$ are essential for this method to work satisfactorily. The form of the curve of Θ_M against T has not been established theoretically but qualitative considerations suggest that it will have a small negative slope at fairly low temperatures and will rise at very low temperature in a manner somewhat similar to that found for plots of Θ_D (specific heat) against T. A careful analysis would be necessary if this method were to be applied to materials where an appreciable difference might be anticipated between the Θ_M values at two temperatures of measurement (e.g. measurements at 300°K and 80°K on Si or diamond).

An interesting variation on the above method has been used by Brockhouse (1955) who measured the change with temperature of the intensity of elastically scattered incoherent neutrons from vanadium and determined the Debye temperature by applying the Debye–Waller expression in its appropriate form. (The cross section for incoherent scattering from vanadium is very much larger than that for coherent scattering.) The variation of intensity with temperature in reflection and transmission electron-diffraction patterns has also been used to estimate vibration amplitudes, and hence Debye temperatures, in a number of metals (Coster and van Zouten 1939, Yamaguchi and Katsurai 1948, Menzel-Kopp and Menzel 1955, 1956). The method does not appear to give very accurate quantitative results but interesting qualitative results have been obtained (see § 7.2).

3.4.3. *Measurement of temperature-diffuse scattering (TDS) in powder patterns*†

Measurement of the temperature-diffuse scattering from single crystals can yield sufficient information to permit derivation of the frequency spectrum of the crystal (Born 1942–3, Jacobsen 1955); if the sample is in the form of a powder, experimental measurements are much easier but the amount of information that can be obtained is correspondingly less. Chipman and Paskin (1959 a) have shown that the temperature-diffuse scattering from a cubic powder can be written (for $T > \Theta_M$):

$$I_{\mathrm{TDS}} = Nf^2 \exp(-2M) \left\{ (2M_{\mathrm{D}})\, C_1 + (2M_{\mathrm{D}})^2 \frac{C_2}{2!} + \ldots\ldots (2M_{\mathrm{D}})\, C_l/l! \right\}; \quad . \;.\; . \; (12)$$

N is the number of atoms, f the atomic scattering factor, $2M$ the usual Debye–Waller factor, $2M_{\mathrm{D}}$ a modified Debye–Waller factor, and the C_l's functions that depend on the details of the calculation of the contribution of the lth order phonon process to the TDS. The calculation of the C_l's has been discussed in detail by Paskin (1958, 1959). The values of f^2 and

---

† See note added in proof.

$2M$ can be taken from other results or derived from measurements on the Bragg reflections and then $2M_D$ obtained by comparison of eqn. (12) with experiment. For both copper and lead Chipman and Paskin (1959 a) find that $2M_D < 2M$ and suggest that this may be due to differences in methods of averaging over the velocities of the elastic waves (see § 4). At present the determination of Debye temperatures from TDS is associated with both experimental and theoretical difficulties and it seems that one of the other x-ray methods is to be preferred for this purpose.

Debye temperatures have also been deduced from the change in energy of cold neutrons after being inelastically scattered by solids (Brockhouse (1955), Eglestaff (1959)). These values were actually obtained in preliminary experimental work on inelastic scattering of neutrons and it is clear that future efforts in this field will be devoted to determining the true form of the vibration spectrum without recourse to the Debye approximation.

3.4.4. *Calculation of atomic vibration amplitudes*

The measured B factor (Debye–Waller temperature factor) is related to the mean square displacement of an atom from its average position by

$$B = 8\pi^2\bar{u}^2/3.$$

This equation applies only to monatomic cubic crystals. Using eqn. (8) one can write (Lonsdale 1948):

$$\bar{u}^2 = \frac{4{\cdot}364 \times 10^2 T}{A\,\Theta_M{}^2}\,\psi(x)\ \text{Å}^2$$

where A is the atomic weight ($^{12}C = 12$). Lonsdale (loc. cit.) has given values of $(\bar{u}^2)^{1/2}$ for a number of elements, using tabulated values of Θ_M. Lonsdale has particularly emphasized that even in cubic crystals the vibration amplitudes are not isotropic and has shown how the components in particular directions due to particular elastic waves can be calculated from a knowledge of the elastic constants. Measurements of integrated diffracted intensity (or TDS from powder samples), to which attention has been restricted here, give only the average vibration amplitude without permitting distinctions among directions in the crystal lattice.

3.5. *Measurements using the Mössbauer Effect*

3.5.1. *Introduction*

There is often an appreciable probability that the γ-ray emitted from a nucleus in a crystal lattice will have the exact energy of the nuclear transition because the recoil energy of the emitting atom will be taken up by the lattice of the host crystallite. As a similar situation can occur on absorption, resonance is obtained if emitting and absorbing nuclei are under identical conditions. Resonant absorption of recoilless γ-rays was first demonstrated by Mössbauer (1958 a, b, 1959) using the 129 kev γ-ray of ^{191}Ir, while more recent work has shown that similar effects occur in a number of other nuclei, including ^{57}Fe, ^{119}Sn and ^{197}Au. The line width is so narrow that resonance can be destroyed by the (first-order) Doppler shift resulting from a small uniform relative velocity of the order of millimetres per second between source and absorber. Accurate measurements of line shapes and positions can be made in this way. Conditions are particularly favourable for ^{57}Fe and an energy resolution of about 1 part in 10^{12} can be obtained for the 14·4 kev γ-ray from this nuclide. This remarkable resolving power has led to the execution of a number of striking experiments, including measurements of the gravitational red shift (Pound and Rebka 1960 b) and other tests of the general theory of relativity (Sherwin 1960) and has also made possible measurement of the electrical and magnetic fields at nuclei in solids. A comprehensive review of theory and applications of the Mössbauer effect has been given by Cotton (1960) while less detailed accounts have been given by Burcham (1960) and Lustig (1961). For present purposes the important feature of the Mössbauer effect is that it provides a number of different ways of measuring the vibration amplitudes of the emitting (or absorbing) nuclei, which are discussed in more detail below.

3.5.2. *Measurements of fraction of recoilless γ-rays emitted or absorbed*

For a nucleus bound in a crystal lattice, the probability of emission or absorption of a γ-ray without energy transfer to or from the lattice is governed by the Debye–Waller factor familiar from diffraction experiments. Thus measurement of the fraction of γ-rays emitted or absorbed without recoil will give the Debye temperature of the lattice. A simplified account of the theory has been given by Lipkin (1960) and more detailed derivations by Visscher (1960) and Singwi and Sjölander (1960). We shall give here a simplified summary of the results of these calculations, following the paper by Singwi and Sjölander. If the emitter and absorber are identical but at different temperatures T_e and T_a and moving with a uniform relative velocity v, then the self-absorption cross section for a crystal with a cubic Bravais lattice is given by

$$\sigma_\mathrm{a}(s) = \frac{\pi\sigma_0\Gamma}{2}\exp\left[-(2W_\mathrm{e}+2W_\mathrm{a})\right] \times \left\{\frac{\Gamma}{\pi}\frac{1}{s^2+\Gamma^2} + \sum_{n=1}^{\infty}\frac{(2W_\mathrm{e}+2W_\mathrm{a})^n}{n!}\bar{g}_n(s)\right\}: \quad . \quad . \quad . \quad (13)\dagger$$

In this expression $s=(v/c)E_0$ where E_0 is energy of the γ-ray emitted, σ_0 is the resonance absorption cross section, Γ is the natural width of the excited state of the nucleus, $\bar{g}_n(s)$ are functions given in detail by Singwi and Sjölander and which are not required for the present discussion.

In the Debye approximation

$$2\,W_\mathrm{e} = \frac{E_0}{2mc^2}\cdot\frac{6T_\mathrm{e}}{k\,\Theta_{\mathrm{Me}}{}^2}\psi(x) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

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† It should be noted that the second-order Doppler shift of the lines due to temperature difference between source and absorber (see below) has been neglected in deriving this equation.

with a similar expression for $2W_a$. $\psi(x)$ has been defined previously in eqn. (9). The analogy between eqn. (14) and the Debye–Waller formula for $2M$ (see eqn. (8), remembering that $2M=2B(\sin^2\theta/\lambda^2)$) is clear if one writes the single equation

$$2M=E_R\frac{6T\psi(x)}{k\Theta_M{}^2}. \qquad (15)$$

For X-ray diffraction E_R is the recoil energy given to the free atom by a photon of energy $E(=hc/\lambda)$ scattered through a total angle 2θ. In this case

$$E_R=\frac{E^2}{mc^2}(1-\cos 2\theta)=\frac{2h^2}{m}\frac{\sin^2\theta}{\lambda^2}.$$

For emission of γ-rays the photon of energy E gives a recoil momentum E/c to a free atom of mass m and thus the kinetic energy of recoil is $E^2/2mc^2$.

Equation (13) shows that the absorption cross section consists of a sharp resonance peak of width 2Γ centred about $s=0$. For $T_e=T_a$ the first term is

$$\sigma'(0)=\tfrac{1}{2}\sigma_0\exp(-4W).$$

The resonance self-absorption cross-section is thus diminished by a factor $\exp(-4W)$. Measurements of the self-absorption cross section will therefore give the Debye temperature at the temperature of measurement. A number of measurements of this type have been made on α–Fe using the 14·4 kev γ-ray from ^{57}Fe. In the earlier experiments agreement between theory and experiment was rather poor (for example Pound and Rebka (1959) reported that only about 20% of the emitted γ-rays were recoilless, whereas the calculated fraction is 72% for $\Theta=355$ °K). More recent work has increased the experimental value to 60% (Cordey-Hayes *et al.* 1960, Clark and Robson 1960) although the fractions of recoilless emissions and absorptions are still less than would be predicted by the Debye model with $\Theta_D=420$°K. Rather similar discrepancies have been reported for measurements on Au, Pt, Ir and Os (Nagle *et al.* 1960). It has sometimes been suggested that these discrepancies are due to real differences between Θ_M and Θ_D for the materials investigated. However, both theory and experiment show that the differences between Θ_M and Θ_D values are seldom greater than 5% and the discrepancies reported must be ascribed to other effects. These may be partly a result of experimental difficulties but it has also been suggested (Bussieré de Nercy, Langevin and Spighel 1960) that Lamb's theory (1939) predicts too large values for the fraction of recoilless emissions or absorptions when the lifetime of the excited state is larger than the time for de-excitation of the lattice.

It is not essential that emitter and absorber should be at the same temperature. In one of his original experiments Mössbauer (1958 a) determined the variation of the absorption cross section of ^{191}Ir when the absorber was held at 88°K and the source temperature varied between 88°K and 380°K. Visscher (loc. cit.) has shown that these experimental results can be explained if $\Theta = 316$ °K, which is somewhat larger than the specific heat value of $\Theta_D = 285$ °K.

The higher-order terms in eqn. (13) give the shape of the wings to the sharp resonance absorption line. If $2W \ll 1$ then all terms in the sum except the first are negligible. In this case, as Visscher has pointed out, the shape of the wings is related in a simple way to the energy spectrum of the crystal vibrations. The experimental situation is, however, rather difficult and it seems probable that slow-neutron scattering provides an easier path to the vibration spectrum.

3.5.3. *Use of second-order Doppler shift of absorption maximum*

An alternative method of deriving Debye temperatures depends on the temperature-dependence of the position of the absorption maximum. The resonance absorption peak will shift because of the change in the energy of the lattice due to the change in nuclear mass consequent on the emission or absorption of a γ-ray photon. The magnitude of this shift has been given by Pound and Rebka (1960 a) and by Josephson (1960) as

$$\frac{\partial \nu}{\partial T} = -\frac{C_P}{2mC^2}$$

where C_P is the specific heat of the lattice at constant pressure. For α-iron the fractional frequency shift will be $2{\cdot}2 \times 10^{-15}/$°K at 300 °K and $0{\cdot}73 \times 10^{-15}/$°K at 80 °K. Pound and Rebka (1960 a) measured $\Delta\nu/\nu$ as a function of the temperature difference between source and absorber and found that their results could be explained if $\Theta_D = 430$ °K. It is worth noting that it is Θ_D which is measured in this experiment, and not Θ_M as in the other Mössbauer effect experiments.

3.5.4. *Rayleigh scattering of Mössbauer radiation*

The methods described above can only be applied to solids containing nuclei which emit suitable γ-rays. However, the method can be extended to other solids by using the high energy discrimination of the Mössbauer effect to measure the fraction of recoilless γ-rays which have been Rayleigh scattered (i.e. without phonon exchange) by a solid at a given temperature (Tzara and Barloutard 1960). This fraction is given by the Debye–Waller factor in the form of eqn. (14). Tzara and Barloutard, using the 23·8 kev radiation from ^{119}Sn and a ^{119}Sn absorber, have determined Debye temperatures of Pt, Al, graphite and paraffin wax in this way and obtained fair agreement with the expected values.

Determination of Debye temperatures by various methods employing the Mössbauer effect may in many instances be simpler than the older techniques. For example Singwi and Sjölander (loc. cit.) have suggested that a change in the absorption of Mössbauer radiation at the superconducting transition temperature could provide experimental evidence for a change in the phonon spectrum at this temperature. Specific heat measurements for Nb have suggested that $\Theta_D \sim 243$°K in the superconducting phase and ~ 231°K in the normal phase (Boorse *et al.* 1960). Earlier neutron diffraction intensity measurements (Wilkinson *et al.* 1954) were able to show that the change in Θ_D could not exceed 20°K. The Mössbauer method would, of course, only be applicable to superconductors with suitable isotopes. In the case of disordered alloys, use of the Mössbauer effect should give information about the vibration amplitudes of the emitting (or absorbing) atoms which cannot be obtained by diffraction measurements (see § 3.9).

At the time of writing (February, 1961) most experiments using the Mössbauer effect for determining Debye temperatures have been essentially exploratory and no accurate values of Θ_M have yet been reported by this technique. But the subject is still in its infancy and one must expect many striking developments in the future.

3.6. *Resistivity Measurements*

Using the Bloch (1928, 1929) theory of the temperature dependence of the electrical resistivity of metals, Grüneisen (1933) related the resistivity to a characteristic temperature Θ_R. In general no close agreement is to be expected between the values of Θ_D and Θ_R as, according to Bloch's theory, Θ_R depends on the longitudinal lattice vibrations only. This was pointed out by Blackman (1951) who, however, noted that there is actually a remarkable correspondence between Θ_R and Θ_D values for many metals. Blackman states: "It is true that the assumptions of the Bloch theory do not apply strictly to most of these cases; why the deviations from these assumptions should lead to $\Theta_R \sim \Theta_D$ is a matter which is in great need of clarification." Because of the lack of a sound theoretical basis for the Θ_R values, they will not be considered further here.

3.7. *Methods Based on Thermal Properties of Crystals*

Because of the dependence of the thermal properties of crystals on the vibration amplitudes of the atoms, it should be possible to derive Θ values from such measured quantities as self-diffusion coefficients, thermal-expansion and conductivity coefficients and melting points. This field has been extensively reviewed by Cartz (1958 b). For example, if the melting point is used, then Lindeman's theory of the melting of a solid can be used to give

$$\Theta = \left[\frac{T_M}{Ar^2 L_r}\right]^{1/2}.$$

Here T_M is the melting point in °K, A is the atomic weight, r is half the distance between neighbouring aroms, and L_r is a constant determined empirically from Θ_D values for F.C.C., B.C.C. and NaCl-type crystals.

Cartz (loc. cit.) used room temperatures values of Θ_D to obtain L_r and found it to vary from the mean value by at most about 20%. Neshpor (1959) has used the thermal characteristics (melting point, Debye temperature, coefficient of linear expansion) to check the various relationships proposed between these quantities. He finds that semi-empirical functions fit the data better than those derived theoretically. For example it was found that

$$\Theta = \frac{12{\cdot}45\, T_M{}^{0\cdot73}\, (C\rho^{2/3})^{1/2}}{M^{1/3}}$$

(C = specific heat in cal/g, ρ = density, M = atomic or molecular weight) fits the data better than the Lindemann formula. No great accuracy can be expected from Θ values derived from the thermal properties of crystals but they are useful when other methods cannot be applied.

3.8. *Other Methods*

Some other methods of deriving Θ values have been discussed by Blackman (1955 a). For ionic crystals infra-red data ('Reststrahlen') and compressibilities can be used but these will not be discussed further as the emphasis in this paper is on metals.

3.9. *Applications to Alloys and Compounds*

Discussion of experimental methods and results in this paper (§§ 6 and 7) has been restricted to cubic elements because inadequacies of the Debye approximation should affect these substances least. The application of the methods described earlier to disordered alloys and ordered compounds (or alloys) should be considered briefly. These applications are of interest because diffraction methods in particular have been widely used in the Soviet Union to determine the effects of various alloying additions on the Debye temperatures of metals; the mechanical properties of the alloys have then been related to the changes in the Debye temperatures and to the static deformations in the alloys (see, for example, Kurdyumov *et al.*, 1955).

The specific-heat and elastic-constants methods of determining Θ_D can be extended to cubic alloys and compounds without difficulties beyond those encountered with the elements, except that the assumption of a monatomic lattice no longer holds for ordered compounds. Debye temperatures can also be calculated formally for non-cubic materials from specific heats or elastic constants but the value of the resulting Θ_D's is limited because the assumptions of the Debye approximation are so far from being fulfilled.

There are some differences when diffraction methods are applied for here one must distinguish between the vibration amplitudes of the individual components. For example, for a disordered binary alloy eqn. (6) must be rewritten (see e.g. Murakami 1953).

$$KF(hkl) = m_A f_A \exp\left(-B_A \frac{\sin^2\theta}{\lambda^2}\right) + m_B f_B \exp\left(-B_B \frac{\sin^2\theta}{\lambda^2}\right) \qquad (16)$$

where m_A, m_B are the atomic fractions of A and B respectively and B_A and B_B their respective temperature factors. The values of B_A and B_B could be obtained by a least squares solution of the observational eqns. (16) but in practice $F(hkl)$ and the atomic scattering factors are seldom known accurately enough for this to be done and the simplifying assumption is made that $B_A = B_B = \bar{B}$. A further complicating factor for disordered alloys is the possible existence of a quasi-temperature factor due to static displacements of the atomic centres from the sites of the average lattice (Herbstein *et al.* 1956, Iveronovna *et al.* 1957, Borie 1957). If this is so, then use of atomic scattering factors to determine $\bar{B}$ will give values which are too large and hence values of Θ_{M} which are too small. Intensity measurements made at two temperatures are necessary for the elimination of this effect. For ordered crystals of stoichiometric composition it is always possible to separate the contribution to $F(hkl)$ from each kind of atom and hence obtain a separate value of B_i for each atom. The Debye approximation is not strictly applicable to ordered crystals because the primitive unit cells are not monatomic but it is possible to derive a value for Θ_{M} if a suitable mean value for B can be found. Lonsdale (1948) has suggested that

$$\bar{B} = W_A B_A + W_B B_B$$

where W_A, W_B are the weight fractions of A, B in the ordered crystal. The experimental results summarized by Lonsdale (loc. cit.) are in reasonable agreement with this suggestion.

Use of the Mössbauer effect promises at least partial alleviation of the difficulties encountered when diffraction methods are applied to disordered alloys. The recoilless emission (or absorption) of γ-rays by an atom depends on the vibration spectrum of the atom in its actual environment in the host lattice. Thus Mössbauer measurements should make it possible to determine the vibration amplitude of the component emitting or absorbing the recoilless γ-ray and thus provide information which cannot at present be obtained from diffraction measurements.

§ 4. THEORETICAL DIFFERENCES BETWEEN DEBYE TEMPERATURES DETERMINED BY DIFFERENT EXPERIMENTAL METHODS

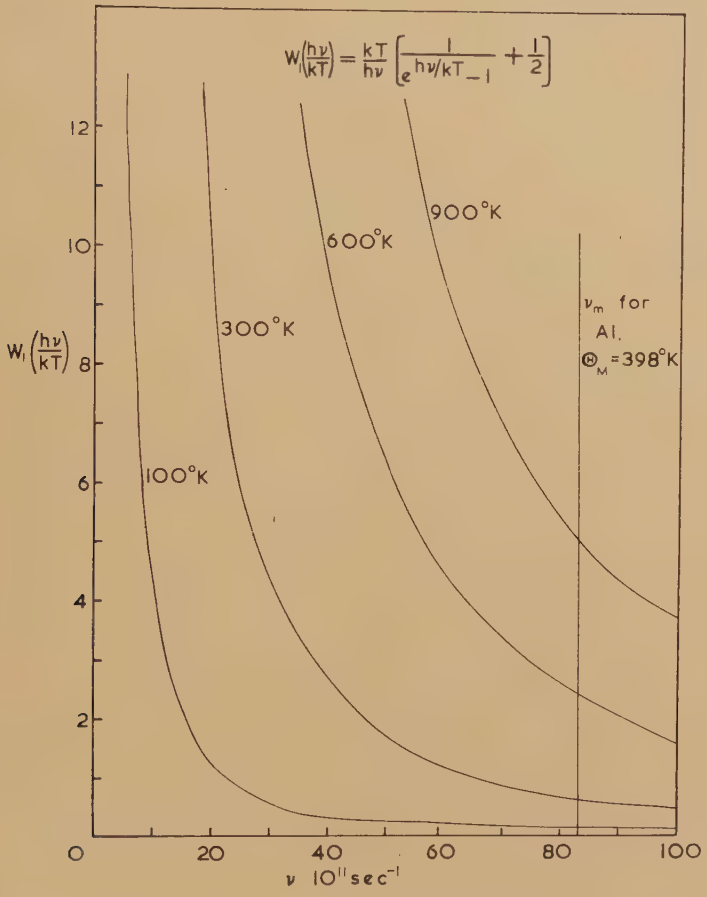
In terms of general frequency distributions the formulae for the Debye–Waller factor (Blackman 1937) and the specific heat can be written:

$$2B = \frac{4h^2}{3NmkT} \sum_{j=1}^{3} \int_0^{\nu_m} N_j(\nu) \left[\frac{1}{p}\left(\frac{1}{e^p - 1} + \frac{1}{2}\right)\right] d\nu, \quad . \quad . \quad (17)$$

$$C_V = k \sum_{j=1}^{3} \int_0^{\nu_m} N_j(\nu) \left[\frac{p^2 e^p}{(e^p - 1)^2}\right] d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where $p = h\nu/kT$ and $N_j(\nu)$ is the frequency distribution function for elastic waves of polarization j. Equations (17) and (18) have been written in the form shown in order to emphasize that a summation over the three types of waves with different polarization vectors must be carried out. The integrands in (17) and (18) both consist of frequency distributions multiplied by weighting factors, denoted by $W_1(h\nu/kT)$ and $W_2(h\nu/kT)$ respectively. These weighting factors are shown in figs. 3 and 4 as functions of frequency and temperature. It is at once apparent that different parts of the frequency distribution are quite differently weighted†, the

Fig. 3



Variation of W_1 $(h\nu/kT)$ with ν and T (see eqn. (17)). The curves of W_1 $(h\nu/kT)\to\infty$ as $\nu\to 0$ but the integrand of (17) is finite at $\nu=0$. The position of Θ_m for Al (Debye approximation) is shown. Thus at 300°K for example, the low-frequency part of the frequency spectrum (below about 30×10^{11} c/s) will make a much larger relative contribution to B than the high frequency portion.

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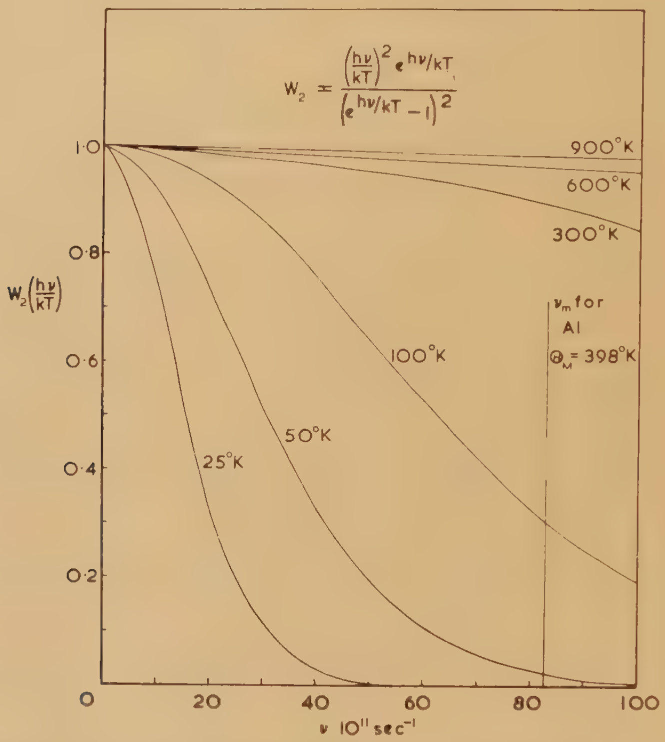
† James (1950, pp. 223–5, especially fig. 75) has previously pointed out that the different frequency ranges of the elastic spectrum make very different contributions to B. James' discussion is in terms of the Debye frequency spectrum.

low-frequency region being relatively much more important for the x-ray temperature factor than for the specific heat. Thus the effects of deviations from a parabolic spectrum on B factors will be different from the effects on specific heats. As the actual frequency spectrum deviates least from a parabolic spectrum at low frequencies, the Debye approximation will fit the x-ray temperature factors better than the specific heats; this should be most marked at low temperatures but unfortunately no experimental data are available to test this prediction. As only the very lowest lattice frequencies are excited in measurements of elastic constants, the Debye approximation will apply accurately to the Θ_D values derived in this way, and deviations from the Debye approximation will not influence the shape of the Θ_D (elastic constants) versus T curve.

Fig. 4



Variation of W_2 $(h\nu/kT)$ with ν and T (see eqn. (18)). This shows that at 300°K for Al all regions of the frequency spectrum make approximately equal relative contributions to C_v.

Parabolic forms for $N_j(\nu)$ must be inserted in (17) and (18) when the Debye approximation is made, i.e. $N_j(\nu)=(9N/\nu_{mj}^3)\,\nu^2$ where ν_{mj} will be different for the transverse and longitudinal modes of vibration. This substitution gives

$$2B=\frac{4h^2T}{mk}\left[\frac{\psi(x_l)}{\Theta_l^2}+\frac{2\psi(x_t)}{\Theta_t^2}\right], \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$C_V=3NkT^3\left[\frac{D(x_l)}{\Theta_l^3}+\frac{2D(x_t)}{\Theta_t^3}\right]; \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where Θ_l and Θ_t are Debye temperatures appropriate to longitudinal and transverse vibrations respectively

$$\text{i.e. } \Theta_l=\frac{h\nu_{ml}}{k}, \qquad \Theta_t=\frac{h\nu_{mt}}{k}$$

$\psi(x)$ has been defined in eqn. (9) and

$$D(x)=\int_0^x \frac{p^4 e^p}{(e^p-1)^2}\,dp$$

is the familiar Debye integral from specific-heat theory. Except at low temperatures the difference between $\psi(x_l)$ and $\psi(x_t)$ will be small; if an average value of Θ_M be chosen such that

$$3\Theta_M{}^{-2}=\Theta_l{}^{-2}+2\Theta_t{}^{-2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

then (19) will become identical with (8). Similar considerations apply to (20); if an average value of Θ_D be chosen such that

$$3\Theta_D{}^{-3}=\Theta_l{}^{-3}+2\Theta_t{}^{-3}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

then (20) will become identical with (2). Zener and Bilinsky (1936) were the first to point out that the average Debye temperatures in (21) and (22) were defined differently and that their ratio could be expressed as a function of Poisson's ratio, using the expressions for Θ_M and Θ_D derived from elastic constants (§ 3.3.1.). Their values of Θ_M/Θ_D are reproduced in table 1. In this paper all numerical values of Debye temperature refer to Θ_D, unless specifically stated otherwise; where necessary, values originally referring to Θ_M have been converted to Θ_D, using table 1. The differences between Θ_M and Θ_D never exceed 7% and are generally about 3–4%.

Table 1. Θ_M/Θ_D as a function of Poisson's ratio σ (from Zener and Bilinsky 1936)

σ	0·25	0·3	0·35	0·4	0·45	0·5
Θ_M/Θ_D	1·025	1·027	1·032	1·040	1·051	1·070

Differences in the methods of averaging over the velocities of the elastic waves also lead to differences between the values of $2M$, the ordinary Debye–Waller factor, and $2M_D$, the corresponding factor for temperature-diffuse x-ray scattering (see § 3.4.3.), with the effect that Θ_M derived from

Table 2. Debye temperatures (Θ_D) of f.c.c. metals

Substance	Temp.	Entropy	Specific heat	Elastic constants		Diffraction measurements		
				c_{ij}	Young's modulus	*f*-curve	Intensities at different temperatures	Temperature diffuse scattering
Ag	0	—	226·0(2)	226·6(2)	—	—	—	—
	300	207(1)	216(3, 4)	216(5)	212(6)	—	212(7)	—
Al	0	—	427·7(8)	428(9)‡	—	—	408 ± 10(11)†	—
	300	379(1)	396(3)	406(9)	402(6)	400(10)	379(12)	—
			380(4)			394 ± 10(11)†	382 ± 10(11)†	—
Au	0	—	164·7(2)	162·1(2)	—	—	—	—
	300	168(1)	185(3, 4)	156(5)	155(6)	—	—	—
Cu	0	—	345·2(2)	344·4(2)	—	—	—	—
	300	304(1)	310(3, 4)	331(13)	326(6)	307(14)†	307(14)†	327(14)
Ni§	0	—	441 ± 15(15)	476(2)	—	—	—	
	300	—	390(15)	460(16)	434(6)	366(17)	341(18)	—
							420(19)	—
Pb	0	—	—	105(20)	—	—	—	
	300	84(1)	93(3)	91(20, 21)	76(6)	82 ± 5(11)†	80 ± 4(11)†	96(14)
							70 ± 4(22)	78(22)
Pd	0	—	274 ± 3(23) 299(24) 275(25, 26) (liquid H_2 range)	275 ± 8(27)	—	—	—	—
	300		280(3)	269(27)	263(6)	—	—	—
Pt	300	—	248(3)	—	225(6)	—	150 ± 26(28)	—
Th	0	—	170(29)	164(2, 30)	—	—	—	—
	300		145(30)	157(30)	159(31)	—	—	—

† TDS under Bragg peaks taken into account.
‡ Extrapolated value.
§ Value of 413–437 °K derived from Mössbauer effect measurements(32).

Bragg intensity measurements would be expected to be lower than that derived from measurements of TDS (Chipman and Paskin 1959 a). Experimental values for Cu and Pb by the two methods (table 2) were in agreement with this expectation but an approximate quantitative treatment suggested that the velocity effects were too small to account for the differences actually found†. Uncertainty as to the theoretical significance of Θ_M from TDS measurements is an added reason for preferring the other diffraction methods of determining Θ_M.

One further consequence of the deviation of the true vibration spectrum from the parabolic form must be mentioned here. The limiting form of the true spectrum at low frequencies is parabolic (Blackman 1955 a, p. 340); the value of Θ_D derived from measurements of elastic constants will be that appropriate to this part of the spectrum. However the x-ray value of Θ_D (i.e. after the correction for the difference between Θ_M and Θ_D has been applied) will be less than the elastic-constant value if the real frequency spectrum rises above its initial parabolic shape. This is because the parabola that fits the true spectrum best over an appreciable part of the total frequency range will be steeper, and thus have a smaller value of ν_m, then the parabola chosen from the limiting shape of $N(\nu)$ at the very lowest values of ν. The rule Θ_D(x-ray) < Θ_D (elastic constants) is a very general one as most real frequency spectra have 'humps' in the lower frequency range (Blackman 1955 b). It is difficult to make a similar prediction for Θ_D (specific heat) as the higher frequencies play a much more important role in determining C_V than B.

§ 5. VARIATION OF DEBYE TEMPERATURE WITH TEMPERATURE

The formal derivations of eqns. (16) and (17) do not require that either the frequency spectrum or the maximum frequency should be invariant with temperature (see Born and Huang 1954, chapter II). As Θ_D depends explicitly on the volume (e.g. Fowler 1955), it is to be expected that it will in turn vary with temperature. Using this volume-dependence of Θ Paskin (1957) has shown that the temperature-dependence of Θ is given by

$$\frac{\Theta(T)}{\Theta(T_0)} = \left[\frac{l(T_0)}{l(T)}\right]^{3\gamma} \quad . \; . \; . \; . \; . \; . \; . \quad (18)$$

where $l(T)$ is the linear dimension of the crystal at temperature T and $l(T_0)$ that at T_0, and γ is Grüneisen's constant ($= V\beta/C_V x$ where β is the coefficient of volume expansion and x the compressibility). This formula is closely equivalent to an earlier formula due to Zener and Bilinsky (1936) which, however, contains less accessible quantities than Paskin's formula. A rather similar formula was given earlier by Owen and Williams (1947), who based their derivation on the Einstein form of the frequency spectrum. The predictions of Paskin's formula are compared with the available experimental data in § 7.2.

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† See note added in proof.

§ 6. The Experimental Results

Values of Debye temperatures at 0°K and 300°K determined by various experimental methods are given in tables 2 (face-centred cubic metals), 3 (body-centred cubic metals), and 4 (diamond-cubic crystals).

The aim in preparing these tables has been to present a comprehensive list of values *for those substances where more than one experimental method has been used.* In general only values from the most recent references are given, and some attempt has been made to select the most reliable results where a number of determinations by the same method are available. Discussions of comparable results are usually given in the references cited and have not been duplicated here.

The results listed are all in terms of Θ_D (see § 4); where the value listed in the original paper was in terms of Θ_M, it has been recalculated here using table 1 and values of Poisson's ratio given by Koster (1954). In many

Table 3. Debye temperatures Θ_D of b.c.c. metals

Substance	Temp.	Entropy	Specific heat	Elastic constants		Diffraction measurements	
				c_{ij}	Young's modulus	*f*-curve	Intensities at different temperatures
Cr	0 300	— —	630(15) 450(33) 405(4)	— —	— 453(6)	— —	— 565(18)
α–Fe	300	—	425(3)	464(34)	467(6)	393(35)	419(69)
Li	0	—	371 at 60°K(36)	335(2)			
	300	365(36)	430(3, 4)	314 at 195°K(37)	357(6) 277(38)	—	341 ± 12(39, 40)
Mo	300	—	370(2) 375(4)	460(41)	443(6)	—	389(18)
Na	0 300	— 146(42)	157 ± 1(43, 44) 155(3) 160(4)	— —	— 180(6)	— —	— 117(45)
V	0	—	338(46) 425 at 20°K(47)	399(48)	—	—	
	300	—	—	389(48) 393(49)	381(6)	—	348 ± 25(51)†
W	0 300	— —	378 ± 7(52) 305(52) 315(4)	— 371(53, 54)	— 364(6)	— —	— —

† Neutron diffraction.

instances the value of Θ_D given in the tables has had to be calculated here from experimental data such as Young's modulus or single-crystal elastic constants; the reference given is then to the experimental data used. A number of the values in the tables differ appreciably from those given by Furukawa and Douglas (1957) in the Handbook of the American Institute of Physics.

The necessity for correcting x-ray determinations of Debye temperature for peaking of temperature-diffuse scattering under the Bragg peaks has been mentioned earlier (§ 3.4.1.); this can only be done when the experimental conditions are known and only those values in the tables marked with an asterisk have been corrected in this way. This correction is not more than a few per cent for Θ_M greater than 300°K, and will always reduce Θ_M below the uncorrected value.

For a number of substances (Al, Pb, Cu, Ag, and Au) it is possible to extend these comparisons of different Θ_D values to cover a wide range of temperatures and these results are given graphically in figs. 5, 6, 7, 8 and 9.

Table 4. Debye temperatures Θ_D of Diamond-type cubic crystals

Substance	Temp.	Entropy	Specific heat	Elastic constants		Diffraction measurements	
				c_{ij}	Young's modulus	f-curve	Intensities at different temperatures
C (diamond)	0	—	2219 ± 20(55) 2246 ± 15(56)	—	—	—	
	300	—	1850(50)	2242(57) 1874(58) 2012(59)	—	1491(60)† 1549(61)†	1990 ± 80(62)†
Si	0	—	636(63) 645 ± 5(68)	649(64)	—	—	—
	300	580(68)	640(68)	647(64)	505(6)	593(65) 522(60)	758(66)
Ge	0	—	363(63) 374 ± 2(68)	374(64, 67)	—	—	—
	300	335(68)	380(68)	371(64, 67)	279(6)	—	—

† Θ_M not Θ_D.

§ 7. Discussion of Results

7.1. Θ_D *Values at* 0° *and* 300°K

It is convenient to discuss the results obtained from related types of experimental measurements first and then to compare the tabulated values by structure type.

The Θ_D values derived from the elastic constants of single crystals, or Young's modulus (E) of polycrystalline samples, can only be satisfactorily compared at 300 °K because of the lack of experimental values of E at very low temperatures (curves of E against temperature have been extrapolated to 0 °K by Koster (1948 a) but it has been felt that these values could not be considered as true experimental determinations and so comparisons have not been made at 0 °K). In general there is agreement between the two sets of values to within 1–2%, with rather larger deviations for Ni (5%) and Mo (4%). Differences are found for Pb (20%), Si (22%) and Ge (25%) and either the c_{ij} or E values must be wrong. For Si and Ge there does not seem to be any possibility of error in the c_{ij} values because of agreement between different authors (McSkimin 1953, Fine 1955) and it seems most likely that the values given for Young's modulus are unreliable. The various values given for Li are also very scattered.

The principal X-ray methods which have been used in practice are (*a*) evaluation of Θ_M from intensities measured at a given temperature by using a theoretical *f*-curve, (*b*) Θ_M from comparison of intensities measured at two or more temperatures. Both methods have been applied to Cu, Ni, Pb, Al, α–Fe, and Si and agreement is good for all these elements except Si. Too few determinations of Θ_M from temperature diffuse scattering alone, or from a combination of TDS and Bragg intensities (Borie's (1956) method), have been made for the capabilities of these methods to be reliably assessed but one would expect Θ_M from TDS alone to be less accurate than the other methods because of the relative weakness of the TDS, the need for correction for Compton scattering and the approximations in the theory. Borie's method is very attractive in principle but the value given for Cu is not very accurate because the TDS had to be treated on the basis of the approximate theory available at the time the work was done†. The different results for silicon illustrate two important points in the application of the X-ray methods: the value of 758°K was obtained from a comparison of intensities at two temperatures, but this comparison was restricted to one reflection and hence it will be very susceptible to experimental errors; this value cannot therefore be considered very reliable. Secondly, two different values were obtained by fitting different *f*-curves to the same set of very accurate intensity measurements (Göttlicher *et al.* 1959, Göttlicher and Wölfel 1959). The *f*-curves used in the first of these references was that due to Viervoll and Ögrim (1949), where electron exchange was not taken into account, while in the second paper the more recent calculations of Freeman (1959), which include the effect of exchange, were used.

The determination of values of Θ_D from specific heats are beset by two main difficulties. At very low temperatures ($T \sim 0$°K) the correction for the electronic specific heat is important and this fact, added to the considerable experimental difficulties of the measurements, makes many reported values unreliable. At higher temperatures ($T > \Theta_D$) the specific heat tends towards the equipartition value of 6 cal/g atom and is not sensitively dependent on the value of Θ_D. There are also theoretical difficulties in interpreting specific heats at relatively high temperatures and so this method is only really useful for $T < \sim \frac{1}{2}\Theta_D$. Although values given in the tables for Θ_D from specific heats refer nominally to 300°K, in fact the values were taken from curves of Θ_D against T at $T = \frac{1}{2}\Theta_D$ (see § 3.1). Many of these values were taken from the curves given by De Sorbo (1954). There are often fairly large differences between Θ_D values at 0°K and those at higher temperatures. This is in qualitative agreement with theoretical calculations based on the Born–von Karman lattice model, which show that Θ_D will be greatest at 0°K.

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† This remark is incorrect—see note added in proof.

One important practical difference between specific-heat and elastic-constant values of Θ on the one hand, and X-ray values, on the other, is that the former are determined at small temperature intervals and thus a detailed curve of Θ_D against temperature can be obtained; the shape of this curve at low temperatures (for specific-heat values of Θ_D) is particularly important for the comparison of experiment with theory. The X-ray values, at least in the past, have been determined at rather wide temperature intervals and further only a few measurements† have so far been reported at temperatures below 80°K.

Strictly speaking, the Θ_D values calculated from the vibrational entropy at 298°K (S_{298}) do not belong in the tables, as they do not refer to a particular temperature of measurement. This is because the entropy is obtained as an integral over the whole temperature range

$$\left(S_{298} = \int_0^{298} \frac{C_P}{T}\,dT\right).$$

It will be noticed that the Θ_D (entropy) values are usually lower than the values obtained from other experimental methods; this is a consequence of the dip in the curve of Θ_D against T at low temperatures which is caused by the discontinuous, lattice nature of the solid. Θ_D values from other methods have not been included in the tables because they do not refer to definite temperatures or because the theoretical position is not clear.

It would be expected that results from the solidified rare gases would be most useful for comparison with theory but experimental measurements are difficult and the only element for which two roughly comparable results are available is Ne. Here specific-heat measurements (Dobbs and Jones 1957) give $\Theta_D = 64$°K at $T \sim 60$ °K, while neutron-diffraction intensity measurements of Bragg peaks at 4°K give $\Theta_M = 73$°K (Henshaw 1958). The Bragg intensities were not corrected for peaking of TDS. It would, of course, be expected that the Debye temperature near absolute zero would be somewhat larger than at higher temperatures.

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† Of these, that for Al at 5 °K (Walker 1956 b) was made as a check only and is not very accurate (private communication from Professor Walker). Renninger (1952) has made intensity measurements on NaCl at 20 °K but these results were not corrected for the peaking of the TDS beneath the Bragg peaks (Nilsson 1957).

A careful comparison has recently been made of elastic-constant (c_{ij}) and specific-heat values of Θ_D at 0°K (Alers and Neighbours 1959) and it has been shown that excellent agreement between the two values is obtained for Cu, Ag and Au. This is also true for Al (Phillips 1959) and Pd (Rayne 1960). The specific-heat values for Ni and Th are less accurate than those for Cu, Ag, Au, Al and Pd but it seems that agreement for these metals is also likely. Good agreement is also obtained for diamond, Si and Ge. All this is in agreement with theory. The agreement for Li is worse but this is probably a consequence of the occurrence of a martensitic transformation (Barrett 1956) at low temperatures. Because of this transformation neither specific heats nor elastic constants of the body-centred cubic form can be measured below about 60°K (Martin 1960 b, Nash and Smith 1959). Extrapolation of the elastic constants to 0°K is not difficult but this cannot be done satisfactorily for the specific heat. Thus a comparison of the two Θ_D values at 0°K is of doubtful validity. No other suitable experimental values have been determined for the substances included in the tables.

The most extensive sets of comparable experimental data available at 300°K are those for Cu, Al and Pb and the agreement is generally good. The elastic-constant values of Θ_D do, however, lie consistently higher than the X-ray results by a few per cent. As mentioned earlier (§ 4) the relation Θ_D (elastic)/Θ_D (X-ray) > 1 is of a very general nature and is due to the existence of peaks in the vibrational spectrum at low frequencies. The only exceptions to this rule noticed in the tables are Cr and Li; in both instances confirmation of the experimental measurements is desirable before a difference in behaviour can be considered as established. The agreement between elastic-constant and some X-ray values of Θ_D for the other face-centred cubic metals is not good: for example for Ni the difference is about 25% (using the values given by Iveronova *et al.* 1951, and Ilyina and Kritskaya 1955 a) and for Pt about 30%. In some instances this may be due to systematic errors in the experimental results. The X-ray methods seem to be particularly liable to experimental errors and one hesitates to accept an X-ray value for Θ_D which has not been independently confirmed. This is illustrated by Ni for which three comparable diffraction measurements of Θ_M have been reported. In the most recent of these experiments (Zhuravlev and Katsnel'son 1959) accurate intensity measurements were made at 215°C, 20°C and −175°C with Mo Kα radiation and a value of Θ_M derived which is in much better agreement with the elastic-constant value than the results reported in the earlier work. It is interesting to note that for Ni Θ_D (elastic constant) > Θ_D (X-ray), in agreement with the results for other elements.

The results for the three diamond-cubic elements (diamond, Si and Ge) provide an interesting pattern of discrepancies and incidentally show how much the accepted experimental values of Θ_D for these elements have changed over the past few years. For diamond the earlier measurements of specific heats seemed to show $\Theta_D \sim 1900$°K at 0°K (Pitzer 1938, De Sorbo 1953) but more recent measurements by Desnoyers and Morrison (1958) and Burk and Friedberg (1958) agree, within combined experimental error, to give $\Theta_D(0°\text{K}) = 2232°\text{K}$. Single-crystal elastic constants have only been measured at room temperature but the three sets of values reported, and the Debye temperatures calculated from them (see table 4) differ considerably. Θ_D calculated from the latest set of values (McSkimin and Bond 1957) is in excellent agreement with the recent specific-heat values†. A value of Θ_M ($= 1990 \pm 80°\text{K}$) has also been obtained from a comparison of X-ray diffraction intensities at 125 °K and 300 °K by Post and Miksic (Post 1960), and this is in good agreement with what would be expected from the specific-heat results. However the values of Θ_M deduced from measurements of intensities at room temperature, using available atomic scattering factors, do not agree well with those given above. The reason for this discrepancy is not clear as two sets of very accurate intensity measurements have been made on diamond (Brill *et al.* 1939, Göttlicher and Wölfel 1959) and the results are concordant. Further, the atomic scattering factors calculated by various authors (Hoerni and Ibers 1954, Berghuis *et al.* 1955, McWeeny 1951, Freeman 1959) are also in good agreement. In their analysis of the experimental results Göttlicher and Wölfel, and Carpenter (1960) (using the measurements by Brill *et al.*), used intensities in the regions

$$0{\cdot}7 < \frac{\sin\theta}{\lambda} < 1{\cdot}3\,A^{-1} \quad \text{and} \quad \frac{\sin\theta}{\lambda} > 1\,A^{-1}$$

respectively so that uncertainties due to the valence-electron distributions were avoided; the small difference in their results is probably due to the slightly different experimental data used. Correction for peaking of TDS under the Bragg peaks would be expected to be small and one may conclude that a value of $\Theta_M = 1520 \pm 60°\text{K}$ (where approximate 95% confidence levels are given) is well established from analysis of X-ray intensities at room temperature with available atomic scattering factors.

Rather similar effects are found for Si. The specific-heat and elastic-constants measurements give Θ_D values which agree excellently at 0°K and 300°K. Accurate measurements of X-ray intensities have been made at 300°K but the difficulty of obtaining an unambiguous X-ray value for Θ_D of Si using atomic scattering factors has been mentioned earlier. If Freeman's (1959) f-curve is accepted because electron exchange was taken into account, then there is a discrepancy of about 20% between the two sets of Θ_D values at 300°K. Presumably the differences found among the various Θ values for diamond and silicon can be accounted for in terms of the real frequency distributions of these elements, but no detailed treatment has been made. It should also be remembered that the diamond lattice is not monatomic. No X-ray measurements have yet been reported for Ge.

The position with regard to α–Fe is as follows. Two different X-ray determinations, one using the f-curve (Herbstein and Smuts 1960) and the other using intensities measured at 300°K and 80°K (Ilyina and Kritskaya 1955 b) are in satisfactory agreement and both sets of measurements were made under suitable experimental conditions. Although the single-crystal elastic constants (see Hearmon (1946) for summary) were measured more than 20 years ago, a number of independent measurements are in good agreement; in addition the values of Θ_D calculated from Young's modulus (Koster 1954) and the c_{ij} agree well. Thus α–Fe appears to be another example where Θ_D (elastic constants) > Θ_D (x-ray).

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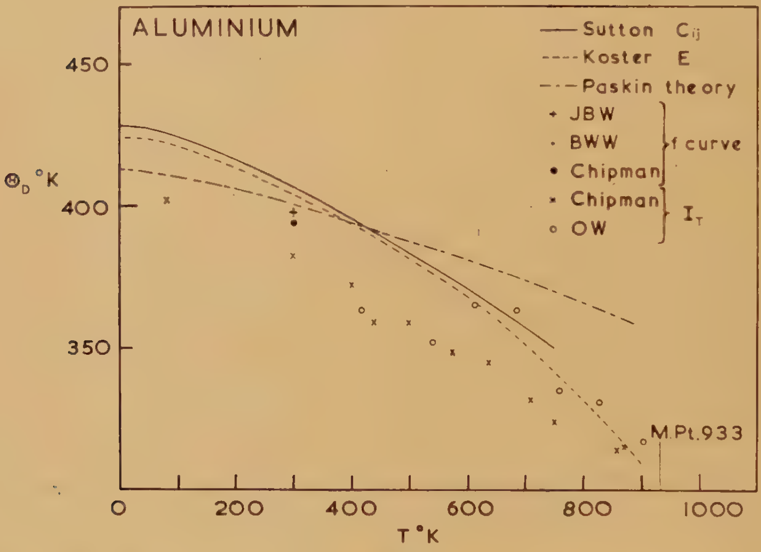
† Because of the high Θ_D of diamond, the elastic constants will hardly change between 300 and 0°K.

A rough picture of the extent of the agreement among the various values of Θ_D reported may be obtained from the fact that for about two-thirds of the examples given in the tables, the deviation of the extreme value from the mean is greater than 10%. Satisfactory agreement (deviation of extreme from mean less than 5%) has been reported only for Cu and Al.

Fig. 5



Variation of Θ_D with T for Al. The references to the values given in the figures are: Sutton 1953, Koster 1948 a, Paskin theory 1957; JBW, James, Brindley and Wood 1929; BWW, Bensch, Witte and Wölfel 1955; Chipman 1960; OW, Owen and Williams 1947.

7.2. *Variation with Temperature*

The most extensive results for the variation of Θ_D with temperature have been given for Al, where values of single-crystal elastic constants (Sutton 1953), Young's modulus (Koster 1948 a), specific-heats (De Sorbo 1954) and x-ray intensities (James *et al.*, 1929, Owen and Williams 1947, and Chipman 1960) between 80°K and about 900°K are available. The Θ_D values calculated from these various experimental measurements are given in fig. 5, together with the curve given by application of Paskin's (1957) method. The two sets of elastic constants give Θ_D values in good agreement with each other up to about 700°K while the X-ray results of Owen and Williams and Chipman are also in reasonably good agreement, with Chipman's results scattering considerably less than those of Owen and Williams. At first sight this agreement is rather surprising as Chipman corrected his results for TDS peaking under the Bragg peaks whereas Owen and Williams' work was done long before the importance of this correction was appreciated. It is possible that their method of intensity measurement was such that the TDS was largely corrected for unintentionally but sufficient details were not given in their paper to judge if this was indeed so.

It should be noted that the Θ_D values from elastic constants are obtained in absolute terms but that the X-ray values determined from the variation of Bragg intensities with temperature will vary according to the value assumed for Θ at some standard temperature, e.g. 300°K. Chipman's values were calculated for $\Theta_D = 382$°K at 300°K, a value which is somewhat lower than the corresponding values obtained using the atomic scattering factor curve for Al. It is therefore possible that the X-ray curve should be shifted upwards by about 13°K, approximately parallel to its present position. The X-ray and elastic-constant values of Θ_D show the same trend with temperature up to about 700°K but above this temperature the values from Young's modulus fall off much more sharply than the X-ray values. It would be desirable to check the variation of Young's modulus with temperature above 700°K. The fact that the temperature variation of Θ_D could not be accounted for in terms of volume changes alone was noted by Owen and Williams and the contrast with their results for Cu and Au emphasized. There is a marked difference in slope between the experimental values and the curve obtained from Paskin's formula.

Fairly extensive data are also available for lead (fig. 6). The absolute difference between the various curves is quite large. The discrepancy between the single-crystal and polycrystal elastic-constant Θ_D values has already been noted. The X-ray results (here fixed along the Θ_D axis by the good agreement between the two X-ray results at 300°K) are closer to the Young's modulus values. Volume changes alone are not sufficient to account for the temperature variations shown.

Rather less detailed results are available for Cu (fig. 7). The X-ray value at 300°K has been determined independently by two groups of workers (Coyle and Gale 1954†, Chipman and Paskin 1959 a) and the agreement is good. This value can be used in turn to obtain values at 80°K from the measurements of Chipman and Paskin, and above room temperature from the measurements of Owen and Williams (1947). The agreement between elastic-constant and X-ray values of Θ_D is not very good. In particular

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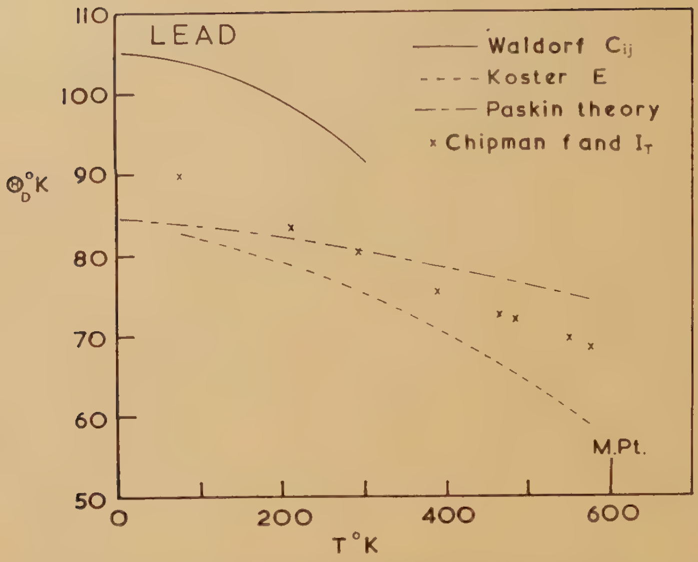
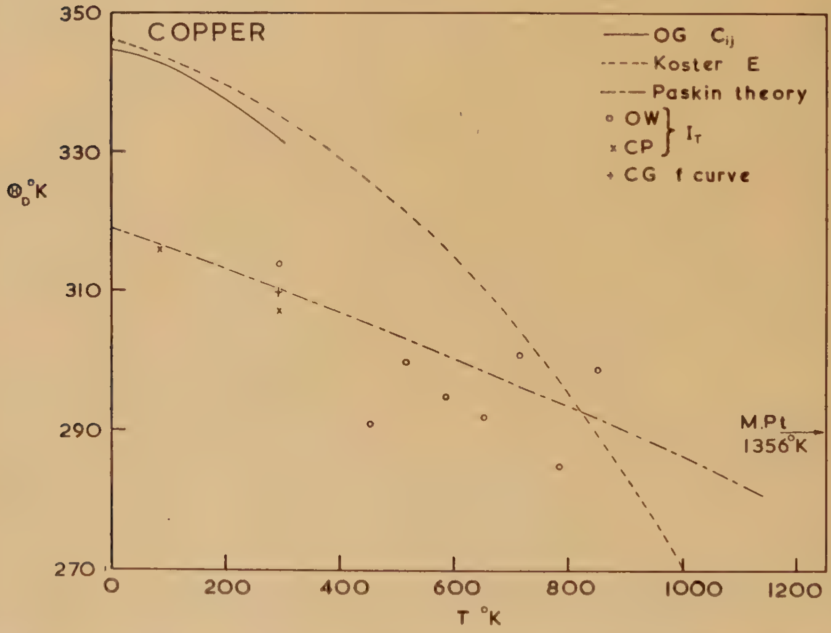
† The original data have been analysed by the author, using newer values of the atomic scattering factors and taking into account peaking of TDS beneath Bragg peaks. The new value of Θ_M is only very slightly different from that given by Coyle and Gale.

Fig. 6



Variation of Θ_D with *T* for Pb. The references are given in the caption to fig. 5 except for Waldorf 1960.

Fig. 7

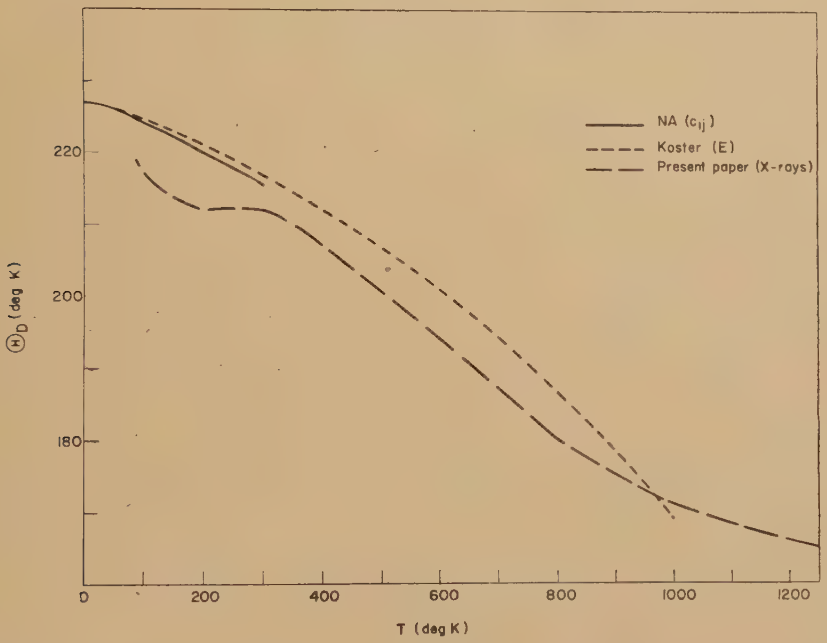


Variation of Θ_D with *T* for Cu. The references to the values given in the figure are: OG, Overton and Gaffney 1955; CP, Chipman and Paskin 1959 a; CG, Coyle and Gale 1954 (also see caption to fig. 5).

the elastic-constant values show a much stronger temperature dependence than the x-ray values, and one may tentatively suggest that this is because the x-ray values of Owen and Williams were not corrected for the TDS under the Bragg peaks. New x-ray measurements above room temperature would be desirable.

Silver has been investigated with x-rays by four groups of workers (Andriessen 1935, Boskovits *et al.* 1958, Spreadborough and Christian 1959, Haworth 1960) and the results reported vary considerably among themselves and also differ appreciably from the Θ_D values derived from measurement of elastic constants. The x-ray results have been re-interpreted (Herbstein 1961) using Chipman's method (1960) and the agreement with the other values (fig. 8) is good. Volume changes alone are not sufficient to account for the temperature variation of Θ_D.

Fig. 8



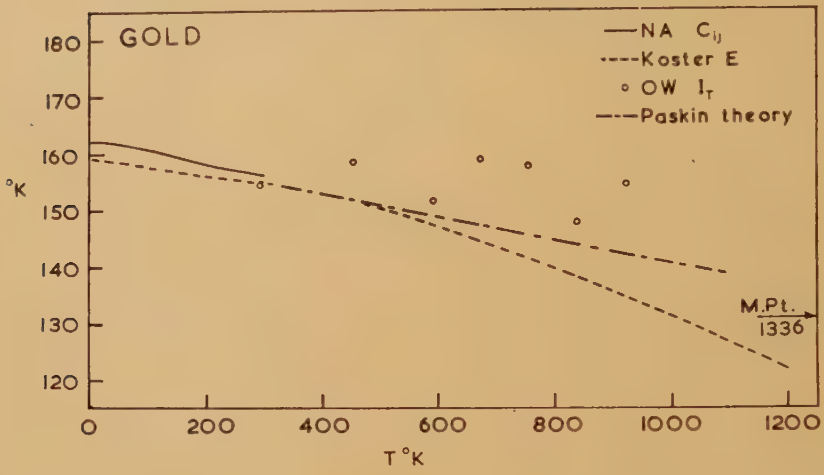
Variation of Θ_D with T for Ag. The references to the values given in the figure are: NA, Neighbours and Alers 1958; H, Herbstein 1961 (also see caption to fig. 5).

X-ray results for Au have only been obtained by Owen and Williams (fig. 9) and the temperature variation of Θ_D can be explained in terms of the effect of volume changes. Again the agreement with the values of Θ_D deduced from the temperature variation of Young's modulus is not very good.

Other experimental results on the temperature variation of Θ_D have been reported for lithium (Alexopoulos 1932, Pankow 1936), sodium (Dawton

1937, 1938) and platinum. The results for the first of these elements show fair agreement between the various methods, while for sodium the agreement is worse. For platinum there is marked disagreement between the x-ray results (Alexopoulos and Euthymiou 1954) and those calculated from Young's modulus. The examples cited in the tables indicate the quality of the agreement for these three metals and detailed diagrams have not been given.

Fig. 9



Variation of Θ_D with T for Au. The references to the values given in the figure are in the captions to figs. 5 and 8.

Electron-diffraction measurements of vibration amplitudes over a range of temperatures have been reported for Au (Coster and van Zouten 1939, Menzel-Kopp and Menzel 1955), Ni (Yamaguchi and Katsurai 1948), Cu (Menzel-Kopp and Menzel 1955, 1956) and Ag (Menzel-Kopp and Menzel 1956). The Debye temperatures derived for Au (Coster and van Zouten) agree reasonably well with the specific-heat values. Menzel-Kopp and Menzel made measurements of vibration amplitudes in Cu and Ag by both reflection and transmission methods. The accuracy of these measurements is not high enough to warrant comparison with the values shown in figs. 7 and 8 but the results are nevertheless of considerable interest because they show that the vibration amplitudes in the surface of the metal (measured by reflection electron diffraction) are considerably larger than those in the bulk of the metal (measured by transmission electron diffraction). The approximation of simple harmonic vibrations is fairly accurate for the bulk of the metal, even near the melting point, but breaks down badly in the surface layers. Rather similar results were reported for Ni.

§ 8. CONCLUSIONS

Of the methods available for determining Debye temperatures, that based on single-crystal elastic constants appears to give the most reliable results as independent measurements are generally, but not always (cf. diamond) in good agreement. Use of Young's modulus is nearly as satisfactory except where difficulties due to large grain size or preferred orientation make interpretation hazardous. Elastic-constant measurements can be conveniently made over the whole temperature range from liquid-helium temperature up to the melting point and at small temperature intervals. They do suffer from the serious disadvantage that only the low-frequency region of the vibration spectrum is involved in the measurement and consequently the curve of Θ_D against T will not provide the information needed for testing frequency spectra derived by more elaborate theoretical or experimental techniques. This information can be obtained from specific-heat measurements, but these will not give accurate Θ_D values at temperatures much above $\frac{1}{2}\Theta_D$. The x-ray diffraction methods have been used fairly widely but difficulties of interpretation remain; for measurements at a given temperature a theoretical atomic scattering factor must be used to derive Θ_M, while measurements over a range of temperatures do not give unambiguous results. The first of these difficulties does not exist for neutron diffraction.

The careful comparison made by Alers and Neighbours (1959) shows that good agreement exists between elastic-constant and specific-heat values of Θ_D at 0°K as required by theory. When this comparison is extended to all available methods over a wide range of temperatures one finds that satisfactory agreement exists only for Al. It does seem that many of the discrepancies encountered may be due to errors of measurement and experimental verification of these discrepancies is desirable before attempts are made to find theoretical reasons for their existence. Nevertheless some large discrepancies between the results of different methods do appear to be established, e.g. for diamond, and there also appears to be definite evidence, shown most strikingly for Cu and Pb, that

$$\Theta_D\,(\text{elastic constants}) > \Theta_D\,(\text{x-ray}).$$

This is in accordance with theoretical expectations (Blackman 1955 b).

For Ag, Al and Pb, the temperature dependence of Θ_D derived from x-ray and elastic-constant measurements is in substantial agreement and cannot be explained by assuming that the changes in Θ_D are due to volume changes only. However, for the other elements for which results are available (Au, Cu), quite different temperature dependences are shown by Θ_D (x-ray) and Θ_D (Young's modulus); the former are in agreement with the theory of the pure volume-dependence of Θ_D while the latter are not. The situation is complicated by the fact that the x-ray measurements were not corrected for the peaking of TDS under the Bragg peaks and it is difficult to estimate the influence of this on the results (see discussion for Al).

At low temperatures no results are available for the variation of Θ_D (x-ray) with temperature, nor has there been any theoretical discussion of this point. When the influence of the weighting factors $W_1(h\nu/kT)$ and $W_2(h\nu/kT)$ (see figs. 3 and 4) is taken into account, it would be expected that Θ_D (x-ray) would be less affected than Θ_D (specific-heat) by deviations of the actual vibration spectrum from the Debye form.

The present survey of experimental results has been restricted to elements because the best agreement among the results of the various experimental methods would be expected for the elements. The discrepancies found have been such that it has not been felt worth while to extend the comparison to alloys, both disordered and ordered, or to salts, because it would be difficult at this stage to decide which effects were due to experimental errors, which to deviations from the Debye approximation and which to the effects of inhomogeneities or long-range order in the materials. Nevertheless it should be remembered that many of the important potential applications of Debye temperatures are to alloy systems for the calculation of such quantities as thermal entropies and x-ray temperature-diffuse scattering.

Despite the 49 years that have elapsed since Debye first proposed his approximate form of the lattice vibration spectrum, its usefulness has not been exhausted, nor indeed is our present knowledge of the Debye temperature, approximate parameter though it may be, adequate for many of the applications required. Many interesting problems remain to be solved and many useful measurements must still be made.

ACKNOWLEDGMENTS

My interest in this field was first stimulated some years ago by Professors B. E. Warren and B. L. Averbach (M.I.T.) and I am grateful for their encouragement. I also wish to thank Dr. J. N. van Niekerk for his support of this work.

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Θ_D values from specific heats, although referred nominally to 300 °K, are actually taken from graphs of Θ_D against T at $T \sim \frac{1}{2}\Theta_D$. The only exception to this rule is diamond (table 4) where Θ_D (300) does refer to 300 °K.

Note added in proof.—Since this paper was submitted (February, 1961) a number of relevant papers have appeared and are discussed below under the appropriate section headings. The literature available in Pretoria to the end of July, 1961 has been covered.

3.3.1. A new summary of elastic constants of the elements (for polycrystalline samples) has been given by Koster and Franz (1961). The values for Young's modulus are generally the same as those quoted in Koster's earlier paper (1954). The only noteworthy change in Θ_D value is for germanium (see table 4). The new value of Θ_D from Young's modulus at 300°K is 313°K, thus reducing but not eliminating the difference between $\Theta_D(E)$ and $\Theta_D(c_{ij})$.

3.4.3. Borie (1961) has shown that the values given by Paskin (1958, 1959) for C_1 and C_2 are not correct and that $2M_D \equiv 2M$ when the Debye model is used. Borie's accurate expression for the temperature-diffuse scattering from a monatomic cubic powder is

$$I_{\mathrm{TDS}} = Nf^2[1-\exp(-2M)] + Nf^2\exp(-2M)(C_1-1)(2M+M^2) \quad \ldots \quad (12a)$$

where the symbols have the same significance as before. C_1 is the function of $\sin\theta/\lambda$ calculated by Warren (1953) for $T > \Theta$ and by Herbstein and Averbach (1955) for all T.

Another method of determining Debye temperatures from diffuse x-ray scattering, first proposed by Cartz (1954), has recently been discussed by Canut and Amorós (1961). The intensity of diffuse scattering at a particular point in reciprocal space depends on the temperature of the crystal; in general the intensity of lth order diffuse scattering first increases as the temperature is raised and then falls. Thus there is a measurable inversion temperature T_{ml} given by

$$T_{ml} = \frac{lk}{3\hbar^2} m\Theta^2 d_{hkl} \quad \ldots\ldots\ldots \quad (12b)$$

d_{hkl} in this expression corresponds to the reciprocal-lattice position at which the measurement was made. Canut and Amorós have used some of Cartz's experimental measurements of T_{ml} for lead to derive $\Theta \sim 90$°K. This method, which is valid for $T > \Theta$ only, should be useful in obtaining approximate values of Θ for crystals, but the exact significance of the value obtained and its relationship to the other types of Θ discussed in this review, will depend to a considerable extent on the exact conditions of measurement.

3.5.1. Three further reviews of Mössbauer effect have appeared (Belozerskiĭ and Nemilov 1961, Shapiro 1961, Mössbauer 1961) and the first two cover the thermal-vibration aspect in some detail. Some of the precautions necessary when comparing values of Θ from Mössbauer experiments with those obtained by other methods are discussed in these papers. Two articles have appeared on the Mössbauer effect in ^{119}Sn. In the first of these (Boyle *et al.* 1960) the frequency shift due to a temperature difference between source and absorber was measured and could be accounted for in terms of the theories of Josephson (1960) and Pound and Rebka (1960 a). In the second paper (Boyle *et al.* 1961) the intensity of the recoilless resonance absorption in tin was measured from 120°K to the melting point. At lower temperatures $\Theta \sim 142^\circ$K but at high temperatures the results indicated considerable anharmonicity of the lattice vibrations.

3.9. A review has appeared on "The Physics of the Strength of Crystalline Materials" (Garber and Gindin 1960), which includes a discussion of Soviet work on thermal-vibration amplitudes in alloys as measures of the strength of interatomic bonding.

6. New measurements have been reported of the single-crystal elastic constants of α-iron (Rayne and Chandrasekhar 1961) over the temperature range 4·2–200°K. The new values agree well with the earlier values for 200°K (Hearmon 1946). The new c_{ij} values give $\Theta_D = 467^\circ$K (at 300°K) compared to 464°K (see table 3). A value of $\Theta_D = 477 \pm 2^\circ$K at 0°K was calculated from the elastic constants by Rayne and Chandrasekhar. Specific heat measurements at very low temperatures (Cheng *et al.* 1960) had been interpreted to give $\Theta_D = 445^\circ$K at 0°K, but Rayne and Chandrasekhar point out that the spin wave contribution to the specific heat was neglected in that analysis. A reasonable value for the spin wave contribution was obtained on the basis of $\Theta_D = 477^\circ$K.

The Debye–Waller factor for copper has been determined from single-crystal x-ray intensity measurements over the temperature range 4·2–500°K (Flinn *et al.* 1961). The results could be interpreted satisfactorily in terms of the frequency spectrum calculated from the central-force model with first and second-neighbour interactions. This paper has been seen in abstract only and it has not been possible to compare the new results with those summarized in fig. 7.

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The Theory of the Interaction of Electrons with Lattice Vibrations in Metals

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§ 1. INTRODUCTION

THE purpose of this article is to present a review of the theory of the interactions of electron and lattice vibrations (phonons) in metals. The only recent reviews in this field are those of Bardeen (1951, 1956). These were largely confined to the special problems that arise in the theory of superconductivity. Our aim, however, will be to present a general review of the field and we shall discuss the problems that arise in both the equilibrium and non-equilibrium properties of a metal. In general we shall not be concerned with the detailed results that emerge when any of these are applied to particular metals. This field has been reviewed in detail by Ziman (1960, 1961). Rather, we shall be concerned with the question of the validity of the methods and the general results that follow from them. We must emphasize that the attitude we take is that fundamentally the so-called electron–phonon problem is one particular aspect of a many-body problem. The many-body problem being that of a number of Fermions (electrons) interacting with the ions that constitute the lattice. If we take this point of view, then not only do we have a many-body problem to deal with but the basic interaction between the particles will be a long-range Coulomb interaction. As is well known, the treatment of such interactions is much more difficult than the short-range interactions that are of importance in electronically saturated systems. We shall see that the Coulomb forces are vital in understanding both the motion of the ions in the lattice and the effective coupling between the moving ions and the electrons.

In § 2 we shall give a qualitative discussion of the physical and theoretical problems in the field. We do this because much of what follows in § 3 is rather technical. This technical discussion is necessary because, if we wish to discuss the validity of the methods that have been used then we must present a reasonably detailed outline of them. Our aim in § 2 will be to avoid the technicalities of the problem and to give a clear physical picture of what the problems are and to describe in qualitative terms the methods that are discussed in § 3. It is hoped that the reader who is not interested in the details of the methods will be able to get a reasonable idea of what they involve by reading this section.

Section 3 is devoted to a fairly detailed exposition of some of the methods that have been used to discuss the problem of electron–phonon coupling in metals. We have been deliberately selective and have chosen for discussion only those methods which seem to us to be important. In fact most of the methods are both in principle and application rather closely related to one another. For this reason the major part of § 3 is devoted to discussing the method used by Nakajima (1953). A much shorter discussion is given of the Born–Oppenheimer (Chester and Houghton 1959) and Hartree–Fock (Toya 1952) methods. The collective coordinate approach (Bardeen and Pines 1955) is only briefly mentioned as a clear description of this method is available in the review article by Bardeen (1956).

In § 4 we discuss the application of the methods reviewed in § 3 to the calculation of thermodynamic functions and transport coefficients. As we have already emphasized, we shall be only interested in the general qualitative features that emerge. We conclude this section by pointing out that for temperatures at or above the Debye temperature of the metal it should be possible to approach the electron–phonon problem by expanding the quantities of interest as a power series in θ/T, where θ is the Debye temperature of the metal.

We finally discuss in § 5 the difficulties that arise when we try to apply any of the methods to the problem of superconductivity. Our main aim will be to give a critical discussion of the validity of the standard methods when applied to this problem. We shall briefly discuss the work of Bogolyubov (Bogolyubov *et al.* 1959) in this field. We conclude this section by pointing out that there are possibly several quite different schemes of approximation available for this particular problem. None of these has as yet been explored.

We now give a brief historical survey of the subject. The first fundamental paper is really that of Bardeen (1937). In this paper he set up the Hartree equations for the metal allowing for the motion of the unscreened ions. Solving these to first order in the ion displacements he showed that the electrons were able to screen the bare Coulomb interaction with the vibrating ions. This self-consistent field method was extended by Toya (1952) to calculate the normal mode frequencies of a metal. The next important step was taken by Fröhlich (1950, 1951, 1952). He pointed out (*a*) that electron–phonon interactions were likely to be the origin of superconductivity—this conjecture was confirmed at the same time by the discovery of the isotope effect (Maxwell 1950 a, b), and (*b*) that the electron–phonon interaction could lead to a phonon self-energy term which would 'renormalize' the lattice frequencies. Fröhlich's work was based on a phenomenological screened interaction and ignored the long-range Coulomb effects. A similar approach was employed by Nakajima (1953). He started from an unscreened interaction and included the Coulomb interaction between the electrons. He found (*a*) that the Coulomb interactions 'screened out' the bare interaction; the effective interaction was identical with that calculated by Bardeen (1937), (*b*) that the longitudinal lattice frequencies were drastically renormalized, and (*c*) that an electron–electron scattering term—corresponding to the exchange of virtual phonons—appeared in the Hamiltonian. This interaction is usually assumed to be responsible for superconductivity. This paper is probably the most important in the whole field and we devote a considerable portion of § 3 to a discussion of it. The methods developed by Bohn and Pines (1952) for an electron gas were extended to take account of the lattice degrees of freedom by Bardeen and Pines (1955). This paper contains a detailed account of the method and we shall not discuss it in this review.

It has recently been proposed (Chester and Houghton 1959) that the parameter $(m/M)^{1/4}$ should be considered as the basic small parameter in electron–phonon coupling problems. This parameter is of course always assumed to be small but it is often assumed that the effective electron–phonon coupling constant is also small. This is a much more dubious assumption. We shall discuss the consequences of this assumption in § 3.3.

Some recent work by Bogolyubov *et al.* (1959) connected with superconductivity will be discussed in § 5.

§ 2. Qualitative Discussion

The conventional physical picture of a metal assumes that the electrons and ions are essentially decoupled from one another. For example, in calculating the specific heat of a metal it is usually assumed that it can be written as the sum of a lattice and electronic part and that any contribution from their interaction is negligible. Again, in calculating the electrical conductivity it is normally assumed that the electrons interact rather weakly with the vibrating lattice and that the scattering by the vibrating lattice can be calculated by perturbation theory. We should say at once that there is a considerable body of experimental evidence which supports this simple picture. On the other hand it is equally certain that it is quite wrong to think in terms of a model of unscreened electrons interacting with unscreened ions in the lattice. Such a model would lead, amongst other things, to an absurdly large electrical resistance due to the strong scattering of the electrons by the long-range Coulomb interactions with the ions. Moreover the frequency spectrum of the longitudinal lattice vibrations would not tend to zero, in the long-wavelength limit, but would tend towards the plasma frequency of the ions. This result is of course quite contrary to what we know experimentally about the frequency spectrum of a metal. What we expect to happen is that the electrons manage to screen out both the Coulomb interactions between themselves and the Coulomb interactions with the vibrating ions. It is just this latter screening problem which is one of the central problems in the theory of the interactions of electrons with lattice vibrations.

On physical grounds we expect that the electrons would try to follow the motion of the ions in such a way as to keep the system locally electrically neutral. For example, when a longitudinal mode propagates in the lattice causing local compressions and rarefactions in the positive ion density we expect that the electrons will try to respond to the motion of the ions in such a way as to screen out the local charge fluctuations. It is in fact very likely that the electrons succeed in doing this. We say 'likely' because there is certainly no convincing theoretical proof that this is so. On the other hand it would be very hard to see why the electrical and thermal resistances of a metal would not be very much greater than they are if this screening did not take place. All the theoretical methods we shall describe in the next section will in fact confirm this statement. If we accept this conclusion for the moment then we would be led to the following tentative 'picture' of a metal. As the ions vibrate and the positive charges are thereby displaced, the electrons respond 'easily' to the forces generated and flow in such a way as to keep the metal locally neutral. Now it is important to realize that the maximum lattice frequency is of the order of $10^{13}\,\mathrm{sec}^{-1}$ and is quite small compared with a typical atomic frequency. This latter frequency is of the order of E_a/h $10^{15}\,\mathrm{sec}^{-1}$ (E_a is of the order of a few electron volts). If the electrons are able to respond in times of the order of atomic times then they will effectively be following the motion of the lattice instantaneously at all frequencies of vibration. In other words the electronic motion will be essentially adiabatic; the wave functions of the electrons adjusting instantaneously to the motion of the ions. The methods we shall describe in § 3 assume that this approximation is valid, except perhaps for a small group of electrons with energies very close to the Fermi energy. We should like to present a simple semi-quantitative argument that confirms this point of view.

What we want to do is to obtain an estimate of the importance of the non-adiabatic terms in the equations of motion. We do this by writing the complete Schrödinger equation in a way which clearly isolates the non-adiabatic terms from the rest. We are then led to an equation of the form

$$\delta\chi_{mn} = \sum_{n'} \frac{C_{nn'}}{E_n - E_{n'}} \chi_{mn'}{}^{(0)},$$

where $\delta\chi_{mn}$ is the lowest order non-adiabatic correction to the wave function and the matrix elements; $C_{nn'}$ are defined by eqns. (2.5), (2.6) and (2.7). The reader who is not interested in the manipulations that lead to this expression for $\delta\chi_{mn}$ can turn at once to the discussion that follows eqn. (2.10). Let us write the exact Hamiltonian of the metal as

$$H = H_{\text{el}} + H_{\text{ion}},$$

where H_{el} is the complete Hamiltonian of the electrons including their interactions with the ions; H_{ion} is the sum of the kinetic and potential energies of the interacting ions. The Schrödinger equation for the electrons with the ions considered to be in fixed positions is then

$$H_{\text{el}}(\mathbf{R})\psi_n(\mathbf{r}|\mathbf{R}) = E_n\psi_n(\mathbf{r}|\mathbf{R}), \qquad \text{(2.1)}$$

where we have written $H_{\text{el}}(\mathbf{R})$ to indicate that the electronic Hamiltonian is parametrically dependent on the positions $\mathbf{R}$ of the ions. Likewise $\psi_n(\mathbf{r}|\mathbf{R})$ indicates that the eigenfunctions also depend on the ion coordinates $\mathbf{R}$. The exact Schrödinger equation for the entire system is

$$H\Phi_m = \mathscr{E}_m\Phi_m. \qquad \text{(2.2)}$$

We can expand Φ_m in terms of the complete set ψ_n

$$\Phi_m = \sum_n \chi_{mn}(\mathbf{R})\psi_n(\mathbf{r}|\mathbf{R}). \qquad \text{(2.3)}$$

If we substitute this expansion into eqn. (2.2) and write the equation in matrix form we find that the χ_{mn} must satisfy (Born and Huang 1954)

$$(T_{\text{ion}} + V_{\text{ion}} + E_n + B_{nn})\chi_{mn} + \sum_{n' \neq n} C_{nn'}\chi_{mn'} = \mathscr{E}_m\chi_{mn}, \qquad \text{(2.4)}$$

where

$$C_{nn'} = A_{nn'} + B_{nn'}, \qquad \text{(2.5}$$

with

$$A_{nn'} = -\frac{\hbar^2}{M}\sum_j \int \psi_n{}^*\nabla_{R_j}\psi_{n'}\,d\tau\,.\,\nabla_{N_j}, \qquad \text{(2.6)}$$

$$B_{nn'} = -\frac{\hbar^2}{2M}\sum_j \int \psi_n{}^*\nabla_{R_j}{}^2\psi_{n'}\,d\tau. \qquad \text{(2.7)}$$

Equation (2.4) is really a matrix operator equation of the form

$$\mathscr{H}\hat{\chi}_m = \mathscr{E}_m\hat{\chi}_m, \qquad \text{(2.8)}$$

where $\hat{\chi}_m$ stands for the column vector $[\chi_{m1}, \chi_{m2}, \cdots \chi_{mn} \cdots]$ and $\mathscr{H}$ is an operator with matrix elements

$$\mathscr{H}_{nn'} = (T_{\text{ion}} + V_{\text{ion}} + E_n + B_{nn})\delta_{nn'} + C_{nn}. \qquad \text{(2.9)}$$

Now if we set $C_{nn'}=0$ then eqn. (2.8) is a diagonal matrix equation and each $\hat{\chi}_m$ that is a solution of it has just one non-zero component. Consequently the wave function $\Phi_m=\chi_{mn}\psi_n$ and is entirely adiabatic. Thus the $C_{nn'}$ are the terms in (2.4) that lead to non-adiabatic motion and we wish to estimate their importance. If we treat them as small then to lowest order we may write

$$\delta\chi_{mn}=\sum_{m'}\frac{C_{nn'}\chi_{mn'}{}^{(0)}}{E_n-E_{n'}}, \qquad (2.10)$$

where $\delta\chi_{mn}$ is the non-adiabatic distortion of the wave function $\chi_{mn}{}^{(0)}$, and $\chi_{mn'}{}^{(0)}$ is a solution of the equation with $C_{nn'}=0$.

Clearly $\delta\chi_{mn}$ will be small as long as the matrix element $C_{nn'}$ is small compared with a typical energy denominator. We do not wish to enter into the details of the estimation of $C_{nn'}$, this is given in Appendix 1, we find that its order of magnitude is $\hbar\bar{v}/l$, where $\bar{v}$ is the average velocity of the ions, and l is the distance through which an ion must be moved to produce an appreciable change in the electronic wave functions ψ_n. The important point to notice is that the energy denominators $E_n-E_{n'}$ will, for most transitions, be of the order of magnitude of the Fermi energy η. This is because the matrix elements $C_{nn'}$ only connect states that differ by single electron excitations and the Pauli exclusion principle forbids all transitions except those from an occupied to an unoccupied state. The great majority of such states have an energy separation of the order of magnitude of the Fermi energy; consequently $E_n-E_{n'}\sim\eta$. This argument obviously breaks down for transitions from just below to just above the last occupied state. However, the number of such states is very small. For if we are a distance δ away in energy from the Fermi level then the number of states is equal to the density of states at the Fermi level multiplied by δ; i.e. of order $(1/\eta)\delta$. Thus the product of the number of states and the energy denominator is of order of magnitude

$$\frac{1}{\eta}\delta\cdot\frac{1}{\delta}$$

and is again of order $1/\eta$. Let us suppose for the moment that this special group of states might also be treated in the same way as those which lie well below the Fermi level. Then

$$\frac{C_{nn'}}{E_n-E_{n'}}\sim\frac{\hbar\bar{v}}{l\eta}.$$

Now $\bar{v}\sim10^5$ cm/sec, $\eta\sim5$ ev and l cannot be much less than 10^{-8} cm. With these values we find

$$\frac{\hbar\bar{v}}{l\eta}\sim2\times10^{-3}.$$

If this estimate is at all reasonable then the non-adiabatic correction to the wave function is extremely small. The essential points in our argument are (*a*) that the Pauli exclusion principle makes transitions with small energy denominators very unlikely and (*b*) that the velocity of the ions is quite small. The estimate we have obtained for the ratio $C_{nn'}/E_n - E_{n'}$ is very similar to that conventionally used for the validity of the adiabatic approximation in electronically saturated systems with discrete electronic levels. In fact (Peierls 1955) the usual criterion differs from ours in that η is replaced by the minimum distance between the discrete levels. Since this distance is usually of the order of electron volts the two criteria are numerically identical. We may put our conclusions in a more picturesque language by saying that the Pauli principle 'freezes out' most of the non-adiabatic transitions and forces the electrons to respond continuously to the motion of the ions. We must now return to the problem of the small group of electrons which lie very close to the Fermi level. The argument we gave to show that these did not contribute abnormally to $\delta\chi_{mn}$ can only be regarded as suggestive. Moreover it is precisely this group of electrons that dominates many physical phenomena. For example, the specific heat and electronic paramagnetism are due entirely to the response of these electrons to thermal and magnetic perturbations. It is therefore of the utmost importance that they be treated very carefully if we are to have any confidence in our results. It seems likely that if a property of a metal depends on the entire distribution of electrons in the Fermi sphere then the non-adiabatic terms in the equations of motion can be safely neglected. Examples of such properties are the cohesive energy and normal mode frequencies. On the other hand properties such as the specific heat and spin paramagnetism could be appreciably modified by the non-adiabatic terms. As far as we are aware none of the present methods of dealing with the electron–phonon interaction problem gives an accurate and convincing treatment of this special group of electrons. We can estimate how close to the Fermi surface we have to be for the adiabatic approximation to break down. If we ask how big $C_{nn'}/E_n - E_{n'}$ has to be for $\delta\chi_{mn} \sim \chi_{mn}^{(0)}$ then we find that

$$|E_n - E_{n'}| \sim \frac{\hbar\bar{v}}{l} \lesssim 10^{-14}\,\text{ergs} \sim \hbar\omega_{\max},$$

where $\omega_{\max}$ is the maximum lattice frequency. We may therefore define a 'danger zone' of electrons that are within $\hbar\omega_{\max}$ of the Fermi energy and any property that depends significantly on these electrons must be calculated taking into account the non-adiabatic terms in the equations of motion. In particular it is very doubtful if any of the current methods gives a sufficiently reliable treatment of them to provide an adequate basis for a theory of superconductivity.

We should now like to give a brief physical description of the methods we shall discuss in detail in § 3. We shall describe three methods, that due to Nakajima, the Born–Oppenheimer method and the Hartree–Fock self-consistent field method. The Hartree–Fock self-consistent field method is essentially no more than a particular way of handling the series of equations generated by the Born–Oppenheimer method and we need say very little about it at this state.

The method due to Nakajima takes into account the long-range Coulomb forces between the electrons and ions. He treats the electrons as moving nearly (but not quite!) adiabatically. They are therefore able to screen out the long-range Coulomb interactions of the ions with each other. The longitudinal mode of vibration of the ions corresponds to the propagation of an ordinary sound wave rather than to the propagation of a plasma wave. The electrons also screen out the Coulomb interaction of the vibrating ions with the conduction electrons; the treatment leads to the usual effective screened matrix element that is used in the theory of electrical conductivity. The other result derived by Nakajima is that the Hamiltonian can be written with a new electron–electron interaction term in it. This term arises from the absorption and emission of virtual phonons by the electrons. These results are obtained by applying a canonical transformation to the Hamiltonian so that the unscreened interaction between the electrons and vibrating ions is removed and replaced by a screened interaction. At the same time the frequency of the longitudinal mode is 'renormalized' so that it becomes well-behaved for long-wavelengths. The important technical point is of course that it is quite impossible to perform the canonical transformation exactly and we have to be content with an approximate expression for the transformed Hamiltonian (see eqn. (3.2)). In § 3 we shall reach the conclusion that the transformed Hamiltonian is very likely to be an accurate approximation for most purposes, but that it may be quite unsound for electrons in the 'danger zone'. The transformed Hamiltonian contains energy denominators that are quite small in this region and even vanish for real (energy conserving) processes in which an electron absorbs or emits a single phonon. This latter defect can be remedied by modifying Nakajima's method to take special account of these real transitions (§ 3.2). This modification does not however remove the difficulty for other transitions in the 'danger zone'. We have already mentioned that the method does not quite treat the electrons as moving adiabatically. The transformed Hamiltonian contains terms which represent both adiabatic and non-adiabatic motion. The latter terms give rise to a large modification of the electronic specific heat. This modification is at present an unobservable effect because it has exactly the same form as the usual electronic specific heat and is therefore indistinguishable from it experimentally.

The basic ideas behind the application of the Born–Oppenheimer method (§ 3.3) to metals are firstly that we expect the motion of the electrons to be largely adiabatic and secondly we wish to make use of the fact that the parameter $\kappa=(m/M)^{1/4}$ is always less than 1/10. The importance of this parameter is that the Born–Oppenheimer method generates a series expansion for all the physical properties of a metal in powers of κ; in fact in most cases in powers of κ^2 rather than κ. This type of expansion immediately opens up the possibility of avoiding expansions in terms of coupling constants which are hardly ever as small as κ and never as small as κ^2. If we did not believe that the motion of the ions is essentially adiabatic then there would be no point in applying this method; it does not yield any non-adiabatic corrections to the energy levels until terms of order κ^6 and the wave functions are adiabatic to order κ^3 (Born and Huang 1954). From what we have said previously it should be clear that this method is also likely to be unsound for electrons in the 'danger zone'. The advantage of the method over Nakajima's lies in that it provides a perfectly systematic approach to the problem. Moreover the expansion parameter κ^2 is really very small and so we may expect fairly rapid numerical convergence of the expansions. Any simple estimate of the convergence always confirms this prediction. Since the method is essentially an adiabtic approximation it produces very similar results to Nakajima's. Only the important difference lies in the fact that Nakajima's method contains non-adiabatic terms in low-order approximations. The large modification to the specific heat therefore does not appear in this method—it can only be obtained by performing a partial summation on the higher-order terms in the series. Both this method and Nakajima's suffer from the technical defect that to carry out the approximations consistently one really has to solve exactly the problem of the conduction electrons moving in the static crystal lattice and interacting via the long-range Coulomb potential. The Hartree–Fock method provides a possible way of approximating to the solution of this basic problem. In fact at each stage of the Born–Oppenheimer method we can solve the appropriate equation by the Hartree–Fock method. We outline this procedure in § 3.4.

We hope that the discussion in this section has provided a reasonable physical picture of the problems involved in the electron–phonon problem. In the next section we shall give a more detailed mathematical discussion of the methods.

§ 3. Basic Methods and Approximations

3.1. *The Basic Hamiltonian*

We begin this section with a discussion of the Hamiltonian of the system. The purpose of this discussion is to show just what approximations are usually made in setting up the Hamiltonian, for, the electron–phonon problem in metals.

We start from the Hamiltonian

$$H_1 = T_{\mathrm{el}} + V_{\mathrm{el}} + T_{\mathrm{nuc}} + V_{\mathrm{nuc}} + V_{\mathrm{int}}. \qquad (3.1)$$

Here we have assumed that the usual non-relativistic approximation is valid—all spin–orbit and spin–spin interactions have been neglected. We believe that these cause no real difficulties and could easily be included in the Hamiltonian. The operators in eqn. (3.1) have the following meanings; T_{el} is the kinetic energy operator for the electrons, T_{nuc} the kinetic energy operator for the nuclei, V_{el} and V_{nuc} are the Coulomb interaction energies of the electrons and nuclei, and V_{int} is the Coulomb interaction energy between electrons and nuclei. It is to be emphasized that all three interaction energies are at this stage assumed to be unscreened Coulomb interactions. The Hamiltonian (3.1) is quite general and contains no specific reference as to whether we are dealing with a metal or not. To overcome this difficulty a more explicit model is usually introduced. The Hamiltonian H_1 is replaced by an approximate one H_2 which represents a collection of ions, rather than bare nuclei, interacting with a sufficient number of electrons so that the whole system is electrically neutral. This implies firstly that the number of electronic degrees of freedom in T_{el} and V_{el} is reduced so that only a small fraction of the total number of electrons contributes to these terms. Secondly that the interaction energies V_{ion} and V_{int} have now to be modified because at small distances of approach the electronic clouds around the nuclei will modify the Coulomb interactions. Both V_{ion} and V_{int} will, however, be Coulomb potentials for large distances of separation. With these explanatory remarks in mind we can write:

$$H_2 = T_{\text{el}} + V_{\text{el}} + T_{\text{ion}} + V_{\text{ion}} + V_{\text{int}}. \quad \quad . \quad . \quad . \quad (3.2)$$

There is little reason to doubt that this approximation to H_1 is sufficiently accurate for almost all purposes.

It is next assumed that there is an equilibrium configuration for the ions and both V_{ion} and V_{int} are expanded in a power series in the displacements of the ions from these equilibrium configurations. More precisely if $F(\mathbf{R}_1 \ldots \mathbf{R}_N)$ is any function of the coordinates $\mathbf{R}_1 \ldots \mathbf{R}_N$ of the ions then we write

$$\begin{aligned} F(\mathbf{R}_1 \ldots \mathbf{R}_N) &= F(\mathbf{R}_1{}^0 + \kappa \mathbf{u}_1, \ldots, \mathbf{R}_N{}^0 + \kappa \mathbf{u}_N) \\ &= F^{(0)}(\mathbf{R}_1{}^0 \ldots \mathbf{R}_N{}^0) + F^{(1)} + F^{(2)} \ldots, \end{aligned}$$

where $F^{(1)}$ is linear in the displacement $\kappa \mathbf{u}_1 \ldots \kappa \mathbf{u}_N$, and $F^{(n)}$ is of the nth order. We have introduced the conventional parameter κ into this expansion; we shall see shortly that our assumptions are only consistent if $\kappa = (m/M)^{1/4}$, where m is the electronic mass and M the ionic mass. Expanding in this way we have,

$$H_2 = \sum_n H_2{}^{(n)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.3)$$

where

$$H_2{}^{(0)} = T_{\text{el}} + V_{\text{el}} + V_{\text{ion}}{}^{(0)} + V_{\text{int}}{}^{(0)}, \quad . \quad . \quad . \quad . \quad (3.4\,a)$$

$$H_2{}^{(1)} = V_{\text{ion}}{}^{(1)} + V_{\text{int}}{}^{(1)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4\,b)$$

$$H_2{}^{(2)} = T_{\text{ion}} + V_{\text{int}}{}^{(2)} + V_{\text{ion}}{}^{(2)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4\,c)$$

$$H_2{}^{(n)} = V_{\text{int}}{}^{(n)} + V_{\text{ion}}{}^{(n)}, \quad n > 2. \quad . \quad . \quad . \quad . \quad (3.4\,d)$$

If $\kappa = (m/M)^{1/4}$ then T_{ion} is of the same degree in κ as $V_{\text{ion}}{}^{(2)}$ and $V_{\text{int}}{}^{(2)}$, and when this is so the simplest equation to determine the motions of the ions is the familiar harmonic equation; it is therefore consistent with the assumption that the ions have an equilibrium configuration. The fact that $\kappa = (m/M)^{1/4} \leqslant 10^{-1}$ for all metals suggests that this expansion scheme may be expected to 'converge' quite quickly. However, it must be borne in mind that some of the effects we are interested in are extremely small—for example, the difference in energy between the normal and superconducting states of a metal is about one part in 10^8—and we should be careful in assuming that *all* the properties of a metal can be calculated from the first few terms in this expansion of H_2. In the methods that we shall review in this section the series (3.3) is truncated at the third term, we call this approximate Hamiltonian H_3:

$$H_3 = H^{(0)} + H^{(1)} + H^{(2)}, \qquad (3.5)$$

where for simplicity we have dropped the suffix 2 on the terms on the right-hand side of this equation. The Hamiltonian H_3 is essentially identical with that used by Bardeen (1956), Nakajima (1953), Toya (1952), Bardeen and Pines (1955) and Chester and Houghten (1959). The only difference is that for many purposes the term $V_{\text{int}}^{(2)}$ in $H^{(2)}$ can be neglected and this has been done by all the authors referred to above. We wish to emphasize that H_3 is a reasonable and consistent approximation to the exact Hamiltonian H_1. It is not however at all clear how justified one is in computing it from quantities which depend on higher powers of κ than the second. This is simply because we have no guarantee that the results of these calculations would not be seriously modified if higher order terms in H were included in the calculations.

It is customary to introduce a number of more technical simplifications in H_3. By this we mean simplifications that are made in the detailed structure of the terms in H_3—particularly simplifications connected with the band structure of the one-electron states. These are usually necessary before any but the most laborious calculations can be made. We first remark that it is convenient to re-define the three interaction terms V_{ion}, V_{el} and V_{int} in H_3 so that each of them is by itself finite. The point here is that each of them is Coulomb-like at large distances of separation and consequently each of them contains an infinite electrostatic energy. The three infinite terms of course exactly cancel one another but it simplifies our considerations if we simply subtract from each interaction the infinite self-energy; the sum of three subtraction terms is of course zero and H_3 is unaltered. With this subtraction procedure each interaction term is itself finite. The simplifications that we shall make to H_3 are most easily formulated in terms of a representation for the operators. We therefore introduce a second quantization scheme for the electron degrees of freedom, using the one-electron Bloch states of the electron moving in the static crystal potential $V_{\text{int}}^{(0)}$† as the basic states.

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† An alternative set of states would be the solution of the Hartree–Fock equation for an electron moving in the lattice. This set of states however probably has the defect that it partially includes the effect of the long-range Coulomb interactions and unless careful account if taken of the remaining part of the Coulomb interactions it could lead to absurd results.

The lattice degrees of freedom are most easily handled in terms of the standard normal coordinates q_f in terms of which we have

$$\kappa\mathbf{u}_j=(NM)^{-1/2}\sum_{\mathbf{f},s}\mathbf{V}_j(\mathbf{f},s)q_{\mathbf{f},s}\exp(i\mathbf{R}_j^0.\mathbf{f}), \quad . \quad . \quad . \quad (3.6)$$

where $\mathbf{f}$ is the usual wave vector, s the polarization index and $\mathbf{V}_j(\mathbf{f},s)$ the set of polarization vectors.

The Bloch wave functions satisfy the equation

$$(t_{\mathrm{el}}+v^{(0)}{}_{\mathrm{int}})\psi_k=\epsilon(k)\psi_k, \quad . \quad . \quad . \quad . \quad (3.7)$$

where t_{el} is the kinetic energy operator for a single electron and $v_{\mathrm{int}}{}^{(0)}$ the static crystal potential for a single electron.

We now write out $H^{(0)}$, $H^{(1)}$ and $H^{(2)}$ explicitly:

$$H^{(0)}=\sum_{\mathbf{k}}a_{\mathbf{k}}{}^*a_{\mathbf{k}}\epsilon(\mathbf{k})+\sum_{\mathbf{kk'f}}V^{\mathrm{C}}_{\mathbf{kk'f}}a_{\mathbf{k'-f}}{}^*a_{\mathbf{k+f}}{}^*a_{\mathbf{k'}}a_{\mathbf{k}}, \quad . \quad . \quad . \quad . \quad (3.8\,a)$$

$$H^{(1)}=\sum_{\mathbf{k},\mathbf{f}}V_{\mathbf{kf}}{}^{(1)}q_{\mathbf{f}}a_{\mathbf{k+f}}{}^*a_{\mathbf{k}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.8\,b)$$

$$H^{(2)}=\tfrac{1}{2}\sum_{\mathbf{f},s}(p_{\mathbf{f},s}{}^2+\Omega_{\mathbf{f},s}{}^2q_{\mathbf{f},s}{}^2)+\sum_{\mathbf{kff'}}V_{\mathbf{kff'}}{}^{(2)}a_{\mathbf{k+f+f'}}{}^*a_{\mathbf{k}}q_{\mathbf{f}}q_{\mathbf{f'}}{}^*. \quad . \quad . \quad (3.8\,c)$$

The sums over $\mathbf{f}$ and $\mathbf{k}$ vectors are to be taken in the extended zone scheme to allow for Umklapp processes (Peierls 1955) and a summation over spin indices is implied in the k summation. The three matrix elements $V^{\mathrm{C}}_{\mathbf{kk'f}}$, $V^{(1)}_{\mathbf{kf}}$ and $V^{(2)}_{\mathbf{kff'}}$ are given by the equations:

$$V^{\mathrm{C}}_{\mathbf{kk'f}}=\iint\psi_{\mathbf{k+f}}{}^*(\mathbf{r}_i)\psi_{\mathbf{k'-f}}{}^*(\mathbf{r}_j)V_{\mathrm{el}}{}^{\mathrm{C}}(\mathbf{r}_i-\mathbf{r}_j)\psi_{\mathbf{k}}(\mathbf{r}_i)\psi_{\mathbf{k'}}(\mathbf{r}_j)\,d^3\mathbf{r}_i\,d^3\mathbf{r}_j, \quad . \quad . \quad (3.9\,a)$$

$$V^{(1)}_{\mathbf{k},\mathbf{f}}=-(NM)^{-1/2}\int\psi_{\mathbf{k+f}}{}^*\left\{\sum_j\mathbf{V}_j(\mathbf{f},s).\nabla_{\mathbf{r}}v_{\mathrm{int}}(\mathbf{r}-\mathbf{R}_j{}^0)\exp(-i\mathbf{f}.\mathbf{R}_j{}^0)\right\}\psi_{\mathbf{k}}\,d^3\mathbf{r}$$
$$. \quad . \quad . \quad (3\,9.b)$$

$$V^{(2)}_{\mathbf{kff'}}=(NM)^{-1}\int\psi_{\mathbf{k+f+f'}}{}^*\left\{\sum_j(\mathbf{V}_j(\mathbf{f},s).\nabla_{\mathbf{r}})(\mathbf{V}_j(\mathbf{f'},s').\nabla_{\mathbf{r}})v_{\mathrm{int}}(\mathbf{r}-\mathbf{R}_j{}^0)\right.$$
$$\left.\times\exp(-i(\mathbf{f}+\mathbf{f'}).\mathbf{R}_j{}^0)\right\}\psi_{\mathbf{k}}\,d^3\mathbf{r}. \quad . \quad (3.9\,c)$$

The frequencies Ω_{fs} that appear in $H^{(2)}$ are the normal mode frequencies of the Hamiltonian,

$$T_{\mathrm{ion}}+V_{\mathrm{ion}}{}^{(2)}.$$

We have omitted the term $V_{\mathrm{ion}}{}^{(1)}$ from $H^{(1)}$ because this term vanishes identically for any periodic lattice (Peierls 1955).

Our first simplification is to assume a monovalent metal with one atom per unit cell. It is a simple matter to extend the formalism to more complicated situations. This means that there are only three values for the polarization index, s.

We assume further that the term

$$\tfrac{1}{2}\sum_{\mathbf{f},s}(p_{\mathbf{f}s}{}^{2}+\Omega_{\mathbf{f}s}{}^{2}q_{\mathbf{f}s}{}^{2})$$

in $H^{(2)}$ can be split into a sum over two transverse modes and one longitudinal. This assumption is of course strictly valid only for very small wave numbers for it is only for these wave numbers that the three modes of vibration have either purely longitudinal or a purely transverse character. However, as many of our most important considerations will refer to these small wave numbers this is a not too drastic approximation.

The frequencies $\Omega_{\mathbf{f}s}$ of the transverse modes tend to zero as $|\mathbf{f}|$ tends to zero. However, the frequency of the longitudinal mode tends to a limiting value

$$(\Omega_{\mathbf{f}})_{\text{long}}\to\left(\frac{4\pi ne^{2}}{M}\right)^{1/2}=\Omega_{p},$$

where Ω_p is the plasma frequency of the ions in the lattice and n is the density of ions. The physical reason for this is that the frequency $\Omega_{\mathbf{f}}$ has been calculated without taking into account the screening of the ions due to the conduction electrons. Consequently the long-range Coulomb forces between the ions dominate the small wave number limit of $(\Omega_{\mathbf{f}})_{\text{long}}$.

A rather more important approximation is that we shall assume that in $V_{\text{int}}{}^{(1)}$ coupling occurs only between the longitudinal mode of vibration and the electrons. This approximation is discussed in detail in Wilson (1953) and Ziman (1960). It is only correct for highly isotropic metals. Nevertheless we shall introduce it to facilitate our calculations—we believe that the qualitative results we shall find will remain valid when coupling to transverse modes is introduced.

Our final simplification is to assume that all the matrix elements of $V^{C}_{\mathbf{kk}'\mathbf{f}}$, $V^{(1)}_{\mathbf{kf}}$ and $V^{(2)}_{\mathbf{kff}'}$ depend only on the difference between the wave vectors of the initial and final states.

We can now use these simplifications to rewrite eqn. (3.8) as

$$H^{0}=\sum_{\mathbf{k}}a_{\mathbf{k}}{}^{*}a_{\mathbf{k}}\epsilon(\mathbf{k})+\sum_{\mathbf{f}}V_{\mathbf{f}}{}^{C}\sum_{\mathbf{k},\mathbf{k}'}a_{\mathbf{k}'-\mathbf{f}}{}^{*}a_{\mathbf{k}+\mathbf{f}}{}^{*}a_{\mathbf{k}'}a_{\mathbf{k}}, \qquad (3.12)$$

$$H^{(1)}=\sum_{\mathbf{f}}V_{\mathbf{f}}{}^{(1)}\sum_{\mathbf{k}}a_{\mathbf{k}}{}^{*}a_{\mathbf{k}-\mathbf{f}}q_{\mathbf{f}}, \qquad (3.13)$$

$$H^{(2)}=\tfrac{1}{2}\sum_{\substack{\mathbf{f}\\ \text{trans}}}(p_{\mathbf{f},s}{}^{2}+\Omega_{\mathbf{f},s}{}^{2}q_{\mathbf{f},s}{}^{2})+\sum_{\mathbf{f},\mathbf{f}',\mathbf{k}}a_{\mathbf{k}}{}^{*}a_{\mathbf{k}-\mathbf{f}-\mathbf{f}'}q_{\mathbf{f}}q_{\mathbf{f}'}V_{\mathbf{f}'}$$
$$+\tfrac{1}{2}\sum_{\mathbf{f}}(p_{\mathbf{f}}{}^{2}+\Omega_{\mathbf{f}}{}^{2}q_{\mathbf{f}}{}^{2}). \qquad (3.14)$$

It follows from the long-range nature of the Coulomb interactions that,

$$V_{\mathbf{f}}{}^{C}\simeq 4\pi e^{2}V^{-1}|\mathbf{f}|^{-2}, \qquad (3.15)$$

$$|V_{\mathbf{f}}{}^{(1)}|\simeq\Omega_{\mathbf{f}}|\mathbf{f}|^{-1} \qquad (3.16)$$

and

$$\Omega_{\mathbf{f}}\simeq(4\pi e^{2}n/M)^{1/2} \qquad (3.17)$$

for small $|\mathbf{f}|$, Bardeen and Pines (1955).

3.2. *The Nakajima Transformation*

In this section we shall describe the canonical transformation introduced by Nakajima (1953) and Bardeen (1956). This transformation is a generalization of the one used by Fröhlich (1952). The basic idea is to transform the Hamiltonian so that the electron and ion degrees of freedom are decoupled to high order of accuracy. The 'largest' coupling term in H_3 is the term $V_{\text{int}}^{(1)}$, this is first order in the ionic displacements. Moreover the matrix element in $V_{\text{int}}^{(1)}$ is unscreened (see eqn. (3.16)) and would lead to entirely wrong temperature dependence for the electrical conductivity. We have already pointed out that the frequency of the longitudinal mode of the ions does not vanish for zero wave numbers; this would lead to an exponential term in the lattice specific heat at low temperatures. The aim of Nakajima's transformation is to (*a*) remove the first-order unscreened coupling term $V_{\text{int}}^{(1)}$ and (*b*) to replace the 'bare' ion frequency $\Omega_{\mathbf{s}}$ by a screened frequency $\omega_{\mathbf{s}}$. It has become customary to refer to the $\Omega_{\mathbf{s}}$'s as the unrenormalized frequencies and the $\omega_{\mathbf{s}}$'s as the renormalized frequencies. It is of course essential that the $\omega_{\mathbf{s}} \sim |f|$, as $|\mathbf{f}| \to 0$, in order that the lattice specific heat have the correct temperature dependence at low temperatures.

We expect on physical grounds (see § 2) that the response of the conduction electrons to the ionic motion screens the moving ions and hence renormalizes the frequency of the longitudinal mode. This implies that any mathematical transformation of H_3 which achieves this renormalization must handle the Coulomb interaction between the electrons to a reasonable approximation. The Nakajima transformation does in fact do this and it is for this reason that we regard it as an important method in the electron–phonon interaction problem. Before describing the transformation we should like to comment on the fact that the method 'transforms away' the unscreened interaction $V_{\text{int}}^{(1)}$. We have already pointed out that in some respects this interaction term has quite the wrong structure and would lead to absurd results for the electrical conductivity. However, it is the only term in H_3 that can lead to real (energy conserving) one-phonon absorption and emission processes, and it is just these processes that we believe give rise to the electrical resistance of an ideally pure metal. Consequently if we transform this term away we are apparently left with no means of accounting for the resistance in terms of real one-phonon processes. An immediate objection to this argument is that if we remove $V_{\text{int}}^{(1)}$ by a canonical transformation then a very similar interaction is likely to reappear in the higher order terms in the transformed Hamiltonian. We shall see however that the new terms which do appear do not have finite matrix elements on the energy shell for one-phonon processes; consequently they cannot lead to a finite resistance. This difficulty with Nakajima's method does not seem to have been discussed in detail before. We show that a simple way round the difficulty is to perform two transformations, one of which is confined entirely to the region of the energy shell for one-phonon processes. The transformation can in fact be chosen so that all the higher order terms are finite on the energy shell and the effective electron–phonon interaction is properly screened.

Nakajima starts from the Hamiltonian H_3 with the term $V_{\text{int}}^{(2)}$ omitted. This term does not contribute to the normal mode frequencies and merely leads to a two-phonon scattering term. Now H_3 can be written in the form

$$H_3 = H^{(0)} + V_{\text{int}}^{(1)} + H_{\text{ph}}^{(r)} + (H_{\text{ph}}^{(b)} - H_{\text{ph}}^{(r)}) + H_{\text{trans}}. \qquad (3.18)$$

Here

$$H_{\text{ph}}^{(r)} = \sum_{\mathbf{f}} (p_{\mathbf{f}}^2 + \omega_{\mathbf{f}}^2 q_{\mathbf{f}}^2) \qquad (3.19)$$

and

$$H_{\text{ph}}^{(b)} = \sum_{\mathbf{f}} (p_{\mathbf{f}}^2 + \Omega_{\mathbf{f}}^2 q_{\mathbf{f}}^2). \qquad (3.20)$$

Both these terms in the Hamiltonian refer only to the longitudinal mode; H_{trans} is the Hamiltonian for the transverse modes. We now transform H_3 by means of a canonical transformation S^N

$$H_3 \to H_3' = \exp(-iS^N) H_3 \exp(+iS^N). \qquad (3.21)$$

We have chosen our units so that $\hbar = 1$. To second order in S_N, H_3' is given by

$$H_3' = H_3 - i[S^N, H_3] - \frac{1}{2!} \,|\, [S^N, [S^N, H_3]]. \qquad (3.22)$$

We choose S_N so that

$$-i[S^N, H^{(0)} + H_{\text{ph}}^{(r)}] + V_{\text{int}}^{(1)} = 0 \qquad (3.23)$$

and the renormalized frequencies $\omega_{\mathbf{f}}$ so that,

$$\frac{i}{2}[V_{\text{int}}^{(1)}, S^N]_{\text{d.p.}} + (H_{\text{ph}}^{(b)} - H_{\text{ph}}^{(r)}) = 0, \qquad (3.24)$$

where the suffix d.p. means that the part of the operator proportional to $q_{\mathbf{f}} q_{\mathbf{f}}^*$ is to be taken. When these two equations are satisfied

$$H_3' = H^0 + H_{\text{ph}}^{(r)} + H_{\text{trans}} + \frac{i}{2}[V_{\text{int}}^{(1)}, S^N]_{\text{n.d.p.}}. \qquad (3.25)$$

where the suffix n.d.p. means that the non-diagonal part is to be taken. This equation is correct to second order in S^N in the following sense. If we count H^0 and $H_{\text{ph}}^{(r)}$ as being of zero order, and $V_{\text{int}}^{(1)}$ as of first order, then (3.23) is consistent. Then $H_{\text{ph}}^{(r)} - H_{\text{ph}}^{(b)}$ must be taken to be of second order if eqn. (3.24) is to be consistent.

If S_N is defined by the equation

$$S^N = i \sum_{\mathbf{k},\mathbf{f}} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} (F(\mathbf{k},\mathbf{f}) q_{\mathbf{f}} - iG(\mathbf{k},\mathbf{f}) p_{\mathbf{f}}), \qquad (3.26)$$

and F and G satisfy the integral equations

$$\begin{aligned}\sum_{\mathbf{k}'} (2V_{\mathbf{f}}^{\text{C}} - V_{\mathbf{k}'-\mathbf{k}}^{\text{C}})(n(\mathbf{k}'-\mathbf{f}) - n(\mathbf{k}'))F(\mathbf{k}',\mathbf{f}) + (W_{\mathbf{k}-\mathbf{f}} - W_{\mathbf{k}})F(\mathbf{k},\mathbf{f}) \\ + (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})F(\mathbf{k},\mathbf{f}) + \omega_{\mathbf{f}}^2 G(\mathbf{k},\mathbf{f}) + V_{\mathbf{f}}^{(1)} = 0,\end{aligned} \qquad (3.27)$$

and

$$\begin{aligned}\sum_{\mathbf{k}'} (2V_{\mathbf{f}}^{\text{C}} - V_{\mathbf{k}-\mathbf{k}'}^{\text{C}})(n(\mathbf{k}'-\mathbf{f}) - n(\mathbf{k}'))G(\mathbf{k}',\mathbf{f}) + (W_{\mathbf{k}-\mathbf{f}} - W_{\mathbf{k}})G(\mathbf{k},\mathbf{f}) \\ + (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})G(\mathbf{k},\mathbf{f}) + F(\mathbf{k},\mathbf{f}) = 0,\end{aligned} \qquad (3.28)$$

where $W_{\mathbf{k}}$ is the usual Hartree–Fock exchange energy,

$$W_{\mathbf{k}} = \sum_{\mathbf{f}'} V_{\mathbf{f}'}{}^{\mathrm{C}} n(\mathbf{k}-\mathbf{f}') \quad . \quad . \quad . \quad . \quad . \quad (3.29)$$

then eqn. (3.23) is satisfied as a matrix equation between any pair of eigenstates of $H^{(0)}$. In eqns. (3.27), (3.28) and (3.29) $n(\mathbf{k})$ is the number operator $a_{\mathbf{k}}{}^{*}a_{\mathbf{k}}$ and should be treated as a diagonal operator in evaluating the commutator in eqns. (3.23) or (3.24). We now examine the transformed Hamiltonian $H_3{}'$. The frequencies ω_s are given implicitly by the eqn. (3.24) which can be written as

$$\omega_{\mathbf{f}}{}^2 - \Omega_{\mathbf{f}}{}^2 = \sum_{\mathbf{k}} F(\mathbf{k},\mathbf{f}) V^{(1)}_{-\mathbf{f}}[n(\mathbf{k}) - n(\mathbf{k}-\mathbf{f})]. \quad . \quad . \quad (3.30)$$

No exact solutions of the integral eqns. (3.27) and (3.28) are known. The approximation that Nakajima made is to ignore the exchange energies $W_{\mathbf{k}}$ and the other exchange terms;

$$\left.\begin{aligned} &\sum_{\mathbf{k}'} V^{\mathrm{C}}_{\mathbf{k}'-\mathbf{k}}(n(\mathbf{k}'-\mathbf{f}) - n(\mathbf{k}'))F(\mathbf{k}',\mathbf{f}) \\ \text{and} \quad &\\ &\sum_{\mathbf{k}'} V^{\mathrm{C}}_{\mathbf{k}'-\mathbf{k}}(n(\mathbf{k}'-\mathbf{f}) - n(\mathbf{k}'))G(\mathbf{k}',\mathbf{f}). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3.31)$$

When this is done the equations can be solved to give

$$G(\mathbf{k},\mathbf{f}) = -\frac{F(\mathbf{k},\mathbf{f})}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.32)$$

and

$$F(\mathbf{k},\mathbf{f}) = \frac{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})v_{\mathbf{f}}}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})^2 - \omega_{\mathbf{f}}{}^2}. \quad . \quad . \quad . \quad . \quad . \quad (3.33)$$

Here

$$v_{\mathbf{f}} = V_{\mathbf{f}}{}^{(1)}[1 + V^{\mathrm{C}}_{\mathbf{f}} S(\mathbf{f})]^{-1} \quad . \quad . \quad . \quad . \quad . \quad (3.34)$$

with

$$S(\mathbf{f}) = \sum_{\mathbf{k}} \frac{n(\mathbf{k}) - n(\mathbf{k}-\mathbf{f})}{\epsilon_{\mathbf{k}-\mathbf{f}} - \epsilon_{\mathbf{k}} + \omega_{\mathbf{f}}}. \quad . \quad . \quad . \quad . \quad . \quad (3.35)$$

The function $v_{\mathbf{f}}$ is usually referred to as the screened matrix element and the factor multiplying $V_{\mathbf{f}}{}^{(1)}$ on the right-hand side of eqn. (3.34) as the screening factor. $S(\mathbf{f})$ is calculated explicitly in Appendix (3) where it is shown to be a rather slowly varying function of $|\mathbf{f}|$. When $|\mathbf{f}|$ tends to zero $S(\mathbf{f})$ tends to a constant, and $v_{\mathbf{f}}$ is for small $|\mathbf{f}|$ given by the equation:

$$v_{\mathbf{f}} = \frac{A|\mathbf{f}|}{B + |\mathbf{f}|^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.36)$$

where A and B are constants. This is exactly the form we would expect for the matrix element if the interaction between the electrons and ions were screened Coulomb interactions rather than bare Coulomb interactions. In § 3.3 we shall see that this approximation to eqn. (3.27) is closely related to the Hartree self-consistent field treatment of the problem.

With the same approximation we find

$$\omega_{\mathbf{f}}^2 = \Omega_{\mathbf{f}}^2 - v_{\mathbf{f}} V_{-\mathbf{f}}^{(1)} S(\mathbf{f}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.37)$$

and for small $|\mathbf{f}|$

$$\omega_{\mathbf{f}}^2 \simeq \frac{\Omega_{\mathbf{f}}^2}{V_{\mathbf{f}}^{\mathrm{C}} S(\mathbf{f})} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.38)$$

This equation implies that $\omega_{\mathbf{f}}$ tends to $c_S|\mathbf{f}|$ for small $|\mathbf{f}|$. In a free electron model this leads to the simple formula,

$$c_S = \frac{1}{\sqrt{3}} \left(\frac{m}{M}\right)^{1/2} v_{\mathrm{F}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.39)$$

where v_{F} is the velocity of the electrons at the Fermi surface and m is the mass of the electrons. This expression for c_S is certainly of the correct order of magnitude. We conclude that this simple approximation leads to results which are certainly qualitatively correct; whether one could trust this approximation quantitatively is a much more difficult question. In §4.1 and §4.2 we shall discuss the quantitative comparison of the above results with experimental data.

The main difficulty in proceeding further with eqns. (3.27) and (3.28) is first that $W_{\mathbf{k}}$ is a fairly complicated function of $|\mathbf{k}|$ and secondly that the terms (3.31) make them non-trivial integral equations. It is necessary to take both these terms into account, to obtain a realistic improvement on the 'Hartree-like' approximation. There have been two attempts to improve on this approximation (Hone 1960, Bailyn 1960). Hone starts from the full set of eqns. (3.27) for F and G. He then makes the approximation of neglecting $\omega_{\mathbf{f}}$ compared with $(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})$. This is for many purposes an accurate approximation because $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}$ will be of the order of the Fermi energy for most transitions whereas $\hbar\omega_{\mathbf{f}}$ can never be greater than a few per cent of this. It is however unlikely that this approximation can be valid always; for example, it is almost certainly a poor approximation if one wishes to calculate an effective electron–electron interaction to introduce into a theory of superconductivity. We shall discuss this point in more detail in § 6.1. When this approximation is carried out eqns. (3.27) reduce to a single integral equation. If we define an effective matrix element $v(\mathbf{k}, \mathbf{f})$ by the equation

$$F(\mathbf{k}, \mathbf{f}) = \frac{v(\mathbf{k}, \mathbf{f})}{E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{f}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.40)$$

where

$$E_{\mathbf{k}} = \epsilon_{\mathbf{k}} - W_{\mathbf{k}}. \quad . \quad . \quad . \quad . \quad . \quad (3.41)$$

Then

$$v(\mathbf{k}, \mathbf{f}) \doteq V_{\mathbf{f}}^{(1)} + \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}', \mathbf{f}) v(\mathbf{k}', \mathbf{f}), \quad . \quad . \quad . \quad (3.42)$$

where

$$A(\mathbf{k}, \mathbf{k}', \mathbf{f}) = \frac{(4V_{\mathbf{f}}^{\mathrm{C}} - V_{\mathbf{k}-\mathbf{k}'}^{\mathrm{C}} - V_{\mathbf{k}-\mathbf{k}'-\mathbf{f}}^{\mathrm{C}}) n(\mathbf{k}')}{E_{\mathbf{k}'-\mathbf{f}} - E_{\mathbf{k}'}} . \quad . \quad . \quad . \quad (3.43)$$

These equations are identical with those derived by Bailyn. His method is to extend the Hartree approximation (Bardeen 1937) for the problem to include the exchange terms. In eqn. (3.42) the sum over the wave vector $\mathbf{k}'$ is weighted with the exact occupation numbers $n(\mathbf{k}')$ for whatever exact state of $H^{(0)}$ we are interested in. In Bailyn's treatment the corresponding sums are to be taken over the unperturbed Fermi distribution $n^0(\mathbf{k}')$. It is of course not known how different the exact occupation numbers $n(\mathbf{k})$ are from the unperturbed ones. The reader is referred to a recent paper by Daniel and Vosko (1960) for a comparison between the unperturbed $n(\mathbf{k})$ and their values for a dense electron gas. It is possible to express the renormalized frequencies directly in terms of $v(\mathbf{k}, \mathbf{f})$:

$$\omega_{\mathbf{f}}^2 = \Omega_{\mathbf{f}}^2 - |V_{\mathbf{f}}^{(1)}|^2 R(\mathbf{f}), \qquad (3.44)$$

where

$$R(\mathbf{f}) = |V_{\mathbf{f}}^{(1)}|^{-1} \sum_{\mathbf{k}} \frac{n(\mathbf{k}-\mathbf{f}) - n(\mathbf{k})}{E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{f}}} v(\mathbf{k},\mathbf{f}).$$

This leads to the following expression for the velocity of sound,

$$c_S = \Omega_0 \lim_{|\mathbf{f}|\to 0} \left[\frac{1 - V_{\mathbf{f}}^{C} R(\mathbf{f})}{4\pi e^2 R(\mathbf{f})} \right]^{1/2}.$$

Both Hone and Bailyn have found approximate solutions of eqn. (3.42). It is not clear how accurate these solutions are in fact; the reader is referred to these papers for the details of the methods used. As we have remarked above, the equation does in principle contain the unknown $n(\mathbf{k})$'s. Hone replaces these by their free electron values and so his equations are finally identical with Bailyn's. One could question whether any major effort should be expended on eqn. (3.42) as long as the $n(\mathbf{k})$'s have to be replaced by what appear to be rather crude approximations.

We next turn to the diagonal part of $[V_{\text{int}}, S_N]$ which is the remaining term in the transformed Hamiltonian. We have

$$\frac{i}{2}[V_{\text{int}}, S^N]_{\text{n.d.p.}} = \sum_{\mathbf{k}\mathbf{k}'\mathbf{f}} V_{-\mathbf{f}}^{(1)} c_{\mathbf{k}'-\mathbf{f}}{}^* c_{\mathbf{k}'} c_{\mathbf{k}}{}^* c_{\mathbf{k}-\mathbf{f}} G(\mathbf{k},\mathbf{f}) + \sum_{\mathbf{f}\mathbf{f}'} M_{\mathbf{f}\mathbf{f}'} q_{\mathbf{f}} q_{\mathbf{f}'} + \sum_{\mathbf{f}\mathbf{f}'} N_{\mathbf{f}\mathbf{f}'} q_{\mathbf{f}} p_{\mathbf{f}'}.$$

The second and third terms on the right-hand side of this equation are two-phonon terms and are likely to be small; no discussion has been given of them in the literature. The first term can be written in the form

$$\sum_{\mathbf{k}\mathbf{f}} \frac{|v_{\mathbf{f}}|^2 n(\mathbf{k})(1 - n(\mathbf{k}-\mathbf{f}))}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})^2 - \omega_{\mathbf{f}}^2} + \sum_{\mathbf{k}\neq\mathbf{k},\mathbf{f}} V^{(1)}{}_{\mathbf{f}} c_{\mathbf{k}'-\mathbf{f}}{}^* c_{\mathbf{k}'} c_{\mathbf{k}}{}^* c_{\mathbf{k}-\mathbf{f}} G(\mathbf{k},\mathbf{f}). \qquad (3.45)$$

The first diagonal term in this expression is exactly what we would have found if we had done second-order perturbation theory with a screened matrix element $v_{\mathbf{f}}$. It is fact identical with the expression used by Fröhlich (1950, 1951) in an attempt to construct a theory of superconductivity. We shall discuss the effect that this term has on the thermodynamic properties of non-superconducting metals in § 4.1. The off-diagonal term has the form of an interaction between the electrons. The interaction arises from the absorption and emission of virtual phonons; is thought (Bardeen 1956) to be responsible for the transition of a metal from the normal to the superconducting state. We remark at this point that it depends, through the frequencies $\omega_{\mathbf{f}}$, on the mass of the ions in the lattice and can therefore in principle at least lead to an isotope effect (Swihart 1957). This term will be discussed further in § 5.

It is clear from the structure of the functions F and G in the Hartree approximation that all the higher order terms in the transformed Hamiltonian will contain energy denominators of the form

$$\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \pm \hbar\omega_{\mathbf{f}}.$$

It is possible to transform the integral equation for $v(\mathbf{k}, \mathbf{f})$ to show that it is a well-behaved function when $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} = \pm\hbar\omega_{\mathbf{f}}$ and consequently even if the more complicated equations for F and G were solved exactly we should still find that all the higher order terms would have the same energy denominators as the Hartree approximation. The appearance of these denominators raises two questions: (*a*) how can we hope to find terms in the transformed Hamiltonian which correspond to real one-phonon processes in which $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} = \pm\hbar\omega_{\mathbf{f}}$ and (*b*) how do these denominators effect the convergence of the series which defines the transformed Hamiltonian The real one-phonon unscreened interaction $V_{\mathrm{int}}^{(1)}$ has been entirely removed from the Hamiltonian, and since both functions F and G become infinite for these transitions it is impossible that any analogous term should appear in the higher order terms in H'. A possible way round this difficulty was first suggested by Fröhlich (1952) and later by Bardeen and Pines (1955). As it has not yet been fully developed in the literature we shall outline the procedure here. The basic idea is that the canonical transformation we have discussed should be carried out for only that part of $V_{\mathrm{int}}^{(1)}$ that lies *off* the energy shells given by the equations:

$$\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} = \pm\hbar\omega_{\mathbf{f}}.$$

It is convenient to split $V_{\mathrm{int}}^{(1)}$ into two parts. We do this by defining a function $\theta(\Delta, \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \pm \hbar\omega_{\mathbf{f}})$ such that

$$\left.\begin{aligned} \theta(\Delta, \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \pm \hbar\omega_{\mathbf{f}}) &= 1 \qquad -\Delta < \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \pm \hbar\omega_{\mathbf{f}} < +\Delta \\ &= 0 \ \text{ otherwise.} \end{aligned}\right\} \qquad (3.46)$$

The parameter Δ defines the width of the shell; we leave it arbitrary for the moment.

Then we can write

$$V_{\text{int}}^{(1)} = U_S + U_{0S}, \qquad \ldots\ldots (3.47)$$

where

$$U_S = \sum_{\mathbf{k},\mathbf{f}} V_{\mathbf{f}}^{(1)} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} q_{\mathbf{f}} \theta(\Delta, \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \pm \hbar\omega_{\mathbf{f}}) \qquad \ldots (3.48)$$

and

$$U_{0S} = \sum_{\mathbf{k},\mathbf{f}} V_{\mathbf{f}}^{(1)} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} q_{\mathbf{f}} (1 - \theta(\Delta, \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \pm \hbar\omega_{\mathbf{f}})). \qquad . (3.49)$$

We now introduce a modified Nakajima transformation $S_N^{(0S)}$ which satisfies the

$$i[S_N^{(0S)}, H^{(0)} + H_{\text{ph}}^{(r)}] + U_{0S} = 0 \qquad \ldots (3.50)$$

and introduce a new transformation S_N^{S} on the energy shell which satisfies

$$i[S_N^{S}, H^{(0)}] + U_S = 0. \qquad \ldots\ldots (3.51)$$

If we set

$$S_N^{0S} = i \sum_{\mathbf{k},\mathbf{f}} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} (F^{0S}(\mathbf{k}, \mathbf{f}) q_{\mathbf{f}} - i G^{0S}(\mathbf{k}, \mathbf{f}) p_{-\mathbf{f}})$$

then eqn. (3.50) is satisfied if F^{0S} and G^{0S} satisfy the equations

$$\sum_{\mathbf{k}'} (2V_{\mathbf{f}}^{\mathrm{C}} - V_{\mathbf{k}'-\mathbf{k}}^{\mathrm{C}})(n(\mathbf{k}' - \mathbf{f}) - n(\mathbf{k}')) F^{0S}(\mathbf{k}', \mathbf{f}) + (W_{\mathbf{k}-\mathbf{f}} - W_{\mathbf{k}}) F^{0S}(\mathbf{k}, \mathbf{f})$$
$$+ (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}) F^{0S}(\mathbf{k}, \mathbf{f}) + \omega_{\mathbf{f}}^2 G^{0S}(\mathbf{k}, \mathbf{f}) + V_{\mathbf{f}}^{(1)}(1 - \theta) = 0 \qquad . . (3.52)$$

and

$$\sum_{\mathbf{k}'} (2V_{\mathbf{f}}^{\mathrm{C}} - V_{\mathbf{k}-\mathbf{k}'}^{\mathrm{C}})(n(\mathbf{k}' - \mathbf{f}) - n(\mathbf{k}')) G^{0S}(\mathbf{k}', \mathbf{f}) + (W_{\mathbf{k}-\mathbf{f}} - W_{\mathbf{k}}) G^{0S}(\mathbf{k}, \mathbf{f})$$
$$+ (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}) G^{0S}(\mathbf{k}, \mathbf{f}) + F^{0S}(\mathbf{k}, \mathbf{f}) = 0. \qquad \ldots (3.53)$$

On the other hand we can satisfy eqn. (3.51) with

$$S_N^{(S)} = \sum_{\mathbf{k},\mathbf{f}} F^{(S)}(\mathbf{k}, \mathbf{f}) q_{\mathbf{f}} \theta a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} \qquad \ldots\ldots (3.54)$$

if $F^{(S)}$ satisfies the equation

$$\{(\epsilon_{\mathbf{k}} - W_{\mathbf{k}}) - (\epsilon_{\mathbf{k}-\mathbf{f}} - W_{\mathbf{k}-\mathbf{f}})\} F^{S}(\mathbf{k}, \mathbf{f}) + 2 \sum_{\mathbf{k}'} V_{\mathbf{f}}^{\mathrm{C}} (n(\mathbf{k}' - \mathbf{f}) - n(\mathbf{k}')) F^{S}(\mathbf{k}', \mathbf{f})$$
$$+ \sum_{\mathbf{k}'} V_{\mathbf{k}'-\mathbf{k}}^{\mathrm{C}} (n(\mathbf{k}') - n(\mathbf{k}' - \mathbf{f})) F^{S}(\mathbf{k}', \mathbf{f}) = V_{\mathbf{f}}^{(1)} \theta. \qquad \ldots (3.55)$$

We can now define the renormalized frequencies $\tilde{\omega}_{\mathbf{f}}$ by the equation

$$\frac{i}{2} [U^{0S}, S_N^{0S}]_{\text{d.p.}} + \frac{i}{2} [U^{S}, S_N^{S}]_{\text{d.p.}} + (H_{\text{ph}}^{(b)} - H_{\text{ph}}^{(r)}) = 0 \qquad (3.56)$$

or more explicitly,

$$\tilde{\omega}_{\mathbf{f}}^2 - \Omega_{\mathbf{f}}^2 = \sum_{\mathbf{k}} F^{0S}(\mathbf{k}, \mathbf{f}) V_{-\mathbf{f}}^{(1)} (1 - \theta) + \sum_{\mathbf{k}} F^{S}(\mathbf{k}, \mathbf{f}) V_{-\mathbf{f}}^{(1)} \theta. \qquad (3.57)$$

From this equation we can see that $\tilde{\omega}_{\mathbf{f}}$ differs from $\omega_{\mathbf{f}}$ by terms of the order

$$\sum_{\mathbf{k},\mathbf{f}} \frac{n(\mathbf{k})\theta}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} - \hbar\omega_{\mathbf{f}}} \simeq \frac{\Delta}{\eta}. \qquad (3.58)$$

Consequently as long as we choose $\Delta \ll \eta$ the new frequencies will differ negligibly from those defined by eqn. (3.37).

The remaining terms in the transformed Hamiltonian are the off-diagonal parts of

$$[S_N^{(0S)}, U_{0S}], \qquad [S_N^{(S)}, U_S],$$

and a one-phonon interaction term

$$[S_N^{(S)}, H_{\mathrm{ph}}^{(r)}] = i \sum_{\mathbf{kf}} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} F^S(\mathbf{k}, \mathbf{f}) p_{\mathbf{f}}^*. \qquad (3.59)$$

The off-diagonal parts of

$$[S_N^{(S)}, U_S]$$

are of exactly the same form as those of

$$[S_N^{(0S)}, U_{0S}]$$

except that they are only non-vanishing on the energy shell defined by eqn. (3.46) and have energy denominators of the form $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}$ instead of $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \pm \hbar\omega_{\mathbf{f}}$. This implies that the residual interaction term between the electrons is quite large. It is however no larger than that given by eqn. (3.45) when $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} \leqslant \hbar\omega_{\mathbf{f}}$. The most significant point about the residual electron–electron interaction terms is that the energy denominators now never vanish. In fact we can let the width Δ of the shell tend to zero in both terms and the final interaction will then be identical with that given by eqn. (3.45) except that the singularity due to the vanishing energy denominator will now be defined to be a principal parts integral.

We now turn to the one-phonon scattering term, eqn. (3.59). It is usually assumed (Wilson 1953) that it is justified to introduce a one-phonon interaction term, with a screened matrix element, into the Hamiltonian of a metal. If we call the screened matrix element $\hat{v}_{\mathbf{f}}$ then the form assumed for the interaction is

$$\sum_{\mathbf{f},\mathbf{k}} q_{\mathbf{f}} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} \hat{v}_{\mathbf{f}}. \qquad (3.60)$$

The interaction (3.59) differs only slightly from this. If we solve eqn. (3.55) in the Hartree approximation and notice (*a*) that on the exact energy shell $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} = \hbar\omega_{\mathbf{f}}$ and (*b*) that the matrix elements of $i\mathbf{p}^*_{\mathbf{f}}/\omega_{\mathbf{f}}$ are the same as those of q_f then the interaction becomes

$$\sum_{\mathbf{k},\mathbf{f}} q_{\mathbf{f}} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} v_{\mathbf{f}} \theta, \qquad (3.61)$$

which is identical with (3.61) on the energy shell if we identify $v_{\mathbf{f}}$ with $\hat{v}_{\mathbf{f}}$. Since $V_{\mathbf{f}}$ is (see eqn. (3.36)) a screened interaction our one-phonon interaction term has just the correct structure. There is however no term in the transformed Hamiltonian corresponding to those parts of (3.61) which lie off the energy shell and consequently there is no justification for the introduction of this interaction term except for energy conserving processes.

We give now a brief discussion of the convergence of the series that defines the transformed Hamiltonian. The convergence of this series is of course the crux of the whole method if the low-order terms in the series give an adequate description of all the physical phenomena we are interested in and high-order terms merely lead to small corrections then the method can certainly be said to be satisfactory. Now we have seen that the terms up to second order (*a*) define a reasonable set of renormalized frequencies, (*b*) give rise to a residual electron–electron interaction that might be used to provide a basis for a theory of superconductivity and (*c*) can lead to a one-phonon scattering term with a screened matrix element. There is thus a distinct possibility that these terms could provide an adequate basis for the phenomena we are interested in. The convergence of the series has never been investigated rigorously and this would be an extremely difficult problem. We can however give a simple qualitative discussion; a similar discussion has been given by Bardeen and Pines (1955). The essential question we have to decide is the order of magnitude of the transformation function S. We can write (compare eqn. (3.26)),

$$S=\sum_{\mathbf{k}} S(\mathbf{k}),$$

where $S(\mathbf{k})$ is the transformation function for an electron with wave vector $\mathbf{k}$. Now the order of magnitude of S is given by

$$|S| \sim \sum_{\mathbf{k}} \sum_{\mathbf{f}} \left| \frac{v_{\mathbf{f}} q_{\mathbf{f}}}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}} \right| n_{\mathbf{k}}(1-n_{\mathbf{k}-\mathbf{f}}).$$

This estimate follows directly from eqns. (3.26) and (3.33), and we have neglected the small term $\tilde{\omega}_{\mathbf{f}}$ in the denominator. We have already seen that we can define the singularity in sums like this by a principal parts procedure. If this description is used then we find $|S| \sim (h\omega_{\text{max}}/\eta)^{1.2}$. This crude estimate is therefore quite satisfactory from the numerical point of view. The whole point however is that in proceeding in this very naive way we have may to treated quite incorrectly those terms $S(\mathbf{k})$ in the sum for S which have small denominators. These terms come of course from electrons in the danger zone. If we have treated those terms incorrectly how reliable is our estimate of the magnitude of S? This question cannot of course be answered rigorously until we are able to treat the electrons in the danger zone correctly. This we cannot do at the moment; what we can do is to show that if these special terms, when treated correctly, do not contribute abnormally to S, then our estimate is at least numerically correct. We show this by simply calculating S with all the terms, whose energy denominators $|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}|$ are smaller than a certain amount ΔE, removed from it. If we call this new function S_E then it is easily shown (see eqn. (3.58)) that,

$$|S^{\Delta}/S| \sim 1 + O(\Delta E/\eta).$$

If $\Delta \ll \eta$ the magnitude of S^{Δ} is identical with that for S. This conclusion is in agreement with what we found earlier for the frequencies; eqns. (3.57), (3.58). It is also in agreement with our qualitative discussion in § 2. On the other hand it should be clear that any prediction we make about the detailed behaviour of this particular group of electrons must be treated with extreme caution. It is in fact believed (Bardeen *et al.* 1957) that it is just these electrons that are involved in the transition from the normal to superconducting states of a metal. If this conjecture is correct then it would be doubtful whether one could base a theory of superconductivity on the lowest order electron–electron interaction term (3.45). We shall discuss this point in more detail in § 5.

3.3. *The Born–Oppenheimer Method*

In this section we shall discuss the application of the Born–Oppenheimer method (Born and Huang 1954) to the electron–phonon coupling problem in metals. We have already discussed in § 2.1 why we believe that this method is likely to be applicable in spite of the breakdown of the standard criterion for its validity. The Born–Oppenheimer method provides a scheme for calculating the wave functions and eigenvalues of a system of nuclei or ions and electrons. It is essentially a type of perturbation expansion in which the expansion parameter is $(m/M)^{1/4}$; the eigenvalues generally contain only even powers of this parameter while the wave functions contain both even and odd powers (Born and Huang 1954). Since this parameter is never greater than 10^{-1} we may expect that these expansions will converge at least numerically. As far as we are able to see this is the only small parameter that is available in the electron-phonon problem and it is for this reason that we believe it is worth while to explore the application of the method to metals.

Again however all our usual reservations must be made about its universal applicability. In particular it is most unlikely to be applicable—at least in its naive form—to the problem of superconductivity. If we take κ as our basic parameter then we shall certainly avoid any reference to the electron–phonon coupling constant which can of course be quite large. We shall see in fact that each term in the Hamiltonian can be easily characterized by a definite power of κ, consequently there is no difficulty at all in generating the formal expansions we require. We should perhaps emphasize that the method is entirely adiabatic until rather high powers of κ are reached in the expansion. To be precise the wave functions are adiabatic up to and including the terms of order κ^2; the eigenvalues up to order κ^4. This implies that the method is quite unsuited to dealing with problems in which non-adiabatic motion is especially important.

The standard method of generalizing the Born–Oppenheimer expansion is rather inconvenient for our purposes because we want to compare it with Nakajima's method. We therefore prefer to generate the low-order terms in the expansion by means of a canonical transformation of the Hamiltonian. The complete expansion can be generated by applying a sequence of canonical transformations to the Hamiltonian. We shall begin by working to order κ^2; we can therefore start from the Hamiltonian H_3. If we transform this Hamiltonian with a canonical transformation S_B defined by the equation

$$i[H_{\mathrm{el}}, S_B] + V_{\mathrm{int}}^{(1)} = 0, \qquad (3.62)$$

then to second order in κ we find that the transformed Hamiltonian H_{3B} is given by

$$H_{3B} = H_{\mathrm{el}} + H_{\mathrm{ph}}^{(b)} + \frac{i}{2}[V_{\mathrm{int}}^{(1)}, S_B] + H_{\mathrm{trans}}. \qquad (3.63)$$

Here we have again dropped the term $V_{\mathrm{int}}^{(2)}$. Equation (3.63) follows directly from (3.62) when we realize that S_B must be of order κ if eqn. (3.62) is to be consistent.

It is a straightforward matter to show (Chester and Houghton 1959) that to order κ^2, H_{3B} gives the same eigenfunctions and eigenvalues as H_3. If

$$S_B = i \sum_{\mathbf{k},\mathbf{f}} a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}} V_{\mathbf{f}}^{(1)} q_{\mathbf{f}} \phi(\mathbf{k}, \mathbf{f}). \qquad (3.64)$$

Then (3.62) is satisfied if

$$\{(\epsilon_{\mathbf{k}} - W_{\mathbf{k}}) - (\epsilon_{\mathbf{k}-\mathbf{f}} - W_{\mathbf{k}-\mathbf{f}})\}\phi(\mathbf{k}, \mathbf{f}) + 2\sum_{\mathbf{k}'} V_{\mathbf{f}}^{\mathrm{C}}(n(\mathbf{k}'-\mathbf{f}) - n(\mathbf{k}'))\phi(\mathbf{k}', \mathbf{f}) \\ + \sum_{\mathbf{k}'} V_{\mathbf{k}'-\mathbf{k}}^{\mathrm{C}}(n(\mathbf{k}') - n(\mathbf{k}'-\mathbf{f}))\phi(\mathbf{k}', \mathbf{f}) = 1, \qquad (3.65)$$

and then

$$\frac{i}{2}[V_{\mathrm{int}}^{(1)}, S_B] = i \sum_{\mathbf{k}} \sum_{\mathbf{f}} V_{\mathbf{f}}^{(1)} V_{-\mathbf{f}}^{(1)} q_{\mathbf{f}} q_{\mathbf{f}}^* \phi(\mathbf{k}, \mathbf{f})[n(\mathbf{k}) - n(\mathbf{k}-\mathbf{f})] \\ + i[V_{\mathrm{int}}^{(1)}, S_B]_{\text{non. diag.}} \qquad (3.66)$$

The first term on the right-hand side of this last equation can be combined with $H_{\mathrm{ph}}^{(b)}$ to give a set of renormalized frequencies ω_B:

$$\omega_B^2 = \Omega_{\mathbf{f}}^2 + \sum_{\mathbf{k}} V_{\mathbf{f}}^{(1)} V_{-\mathbf{f}}^{(1)} \phi(\mathbf{k}, \mathbf{f})[\bar{n}(\mathbf{k}) - \bar{n}(\mathbf{k}-\mathbf{f})]. \qquad (3.67)$$

We can rewrite H_{3B} as

$$H_{3B} = H_{\mathrm{el}} + H_{\mathrm{ph}}^{(r)} + H_{\mathrm{tr}} + \sum_{\substack{\mathbf{k}\mathbf{f} \\ \mathbf{f}' \neq \mathbf{f}}} V_{\mathbf{f}} V_{\mathbf{f}'} q_{\mathbf{f}} q_{\mathbf{f}'} \phi(\mathbf{k}, \mathbf{f})(a_{\mathbf{k}}^* a_{\mathbf{k}-\mathbf{f}-\mathbf{f}'} - a_{\mathbf{k}+\mathbf{f}'}^* a_{\mathbf{k}-\mathbf{f}}). \qquad (3.68)$$

If we compare eqns. (3.64), (3.65) and (3.67) with eqns. (3.26), (3.27) and (3.30), we see that they are very similar indeed. In fact they become identical if we neglect the terms proportional to $\omega_{\mathbf{f}}^2$ in eqn. (3.27); this is the approach used by Hone in his discussion of the effective electron phonon matrix element. As we have pointed out, since $\omega_{\mathbf{f}} \ll |\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}|$ for most transitions, this approximation is likely to be quite accurate. We can easily verify this by solving the eqn. (3.65) in the simple Hartree approximation. We find that

$$\phi(\mathbf{k}, \mathbf{f})(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}) = \frac{1}{1 + 2V_{\mathbf{f}}{}^{C} \sum_{\mathbf{k}'} \left\{ \dfrac{n(\mathbf{k}'-\mathbf{f}) - n(\mathbf{k}')}{\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}'-\mathbf{f}}} \right\}} \qquad (3.69)$$

and hence

$$\omega_B{}^2 = \Omega_{\mathbf{f}}{}^2 + V_{-\mathbf{f}}{}^{(1)} V_{\mathbf{f}}{}^{(1)} \sum_{\mathbf{k}} \frac{\tilde{n}(\mathbf{k}) - \tilde{n}(\mathbf{k}-\mathbf{f})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}}. \quad . \quad . \quad . \quad (3.70)$$

The sum

$$S^0(\mathbf{f}) = \sum_{\mathbf{k}} \frac{\tilde{n}(\mathbf{k}) - \tilde{n}(\mathbf{k}-\mathbf{f})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}}$$

is calculated in Appendix 3, where it is shown that it differs by terms of order $\hbar\bar{\omega}_B/\eta$ from the sum in which the energy denominators are $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} - \hbar\omega_B$. Consequently when we compare the equation for ω_B with eqn. (3.37) for $\omega_{\mathbf{f}}$ we see that they differ by terms and of order $\hbar\omega_B/\eta$; that is to say by at most a few per cent. The screened matrix element $v_{\mathbf{f}}$ is given now by the equation

$$v_{\mathbf{f}} = V_{\mathbf{f}}{}^{(1)} \left[1 + V_{\mathbf{f}}{}^{C} \sum_{\mathbf{k}} \frac{\tilde{n}(\mathbf{k}-\mathbf{f}) - \tilde{n}(\mathbf{k})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}} \right]^{-1}, \quad . \quad . \quad . \quad (3.71)$$

and differs by a few per cent from that defined by the Nakajima transformation.

We see from eqn. (3.68) that to order κ^2, H_{3B} contains no term that could give rise to real one-phonon processes and no terms that represent electron–electron interactions via the exchange of virtual phonons. However, both these terms arise in higher-order terms in H_3. If the Hamiltonian is calculated to third order we find a term

$$i \sum_{\mathbf{k},\mathbf{f}} a_{\mathbf{k}}{}^* a_{\mathbf{k}-\mathbf{f}} V_{\mathbf{f}}{}^{(1)} \phi(\mathbf{k}, \mathbf{f}) p_{\mathbf{f}}{}^*. \quad . \quad . \quad . \quad (3.72)$$

This term gives rise to energy-conserving one-phonon processes and on the energy shell is identical with the usual phenomenological interaction (see eqns. (3.60) and (3.69)). When $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} = \pm\hbar\omega_{\mathbf{f}}$ the matrix elements of this term are of order κ; it is easily seen that all other terms in the Hamiltonian that give rise to real one-phonon processes have matrix elements of higher order in κ. It is therefore consistent to use the interaction (3.72) to calculate the one-phonon scattering. The Born-Oppenheimer method therefore has the advantage that it automatically gives a one-phonon scattering term of the correct structure. This result was first noticed by Ziman (1955) and Goodman (1958).

To order κ^3 no term of the type given by eqn. (3.72) arises but at order κ^4 we do find a term of exactly the type; namely

$$\sum_{\mathbf{k},\mathbf{f}} \frac{n(\mathbf{k})(1 - n(\mathbf{k}-\mathbf{f})) v_{\mathbf{f}}{}^2}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}})^2} + \sum_{\mathbf{k}\mathbf{k}'\mathbf{f}} (\text{off-diag. terms}), \quad . \quad . \quad (3.73)$$

where we have separated the diagonal part of this term from the scattering part. The only difference between these terms and those derived by Nakajima is that the energy denominators contain no phonon energies. We see at once that when $\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}$ is small these terms become very large—larger than those in eqn. (3.45). In particular if we believe that interactions, in which both $\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}-\mathbf{f}}$ are very close to the Fermi energy, are important, then these terms will become exceedingly large. This difficulty is of course the counterpart of the difficulty we found in Nakajima's method where we saw that the method broke down when $\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}-\hbar\omega_{\mathbf{f}}$ became very small.

The convergence of the method is again very difficult to assess; the main difficulty lies in the fact that the amplitude of the transformation S_B becomes very large when $\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}$ is small. By the same argument that we used in § 3.2 if we cut out an energy shell of width Δ then we can expect reasonable convergence if $\Delta \leqslant \eta$.

3.4. *The Hartree–Fock Method*

In this section we shall show how the Hartree–Fock method can be applied to the problem we are interested in. This method was first used by Bardeen (1937) to calculate the effective electron–phonon matrix element. Toya (1952) extended it to obtain the renormalized frequencies. The method—in so far as it has been used to date—really assumes that the adiabatic approximation is valid. We can therefore easily formulate it in terms of the Born–Oppenheimer expansion. The Hartree–Fock method is very easily set up in configuration space and it is therefore convenient to derive the Born–Oppenheimer expansion by the conventional approach (Born and Huang 1954) rather than use a second quantization scheme of § 3.3.

The expansion can be generated very simply using eqns. (2.1)-(2.11). We proceed as follows. First we solve eqn. (2.1) by a perturbation expansion in powers of κ. Thus

$$\psi_n(\mathbf{r}|\mathbf{R})=\sum_s \kappa^s\psi_n^{(s)} \qquad (3.74)$$

$$E_n=\sum_s \kappa^s E_n^{(s)}. \qquad (3.75)$$

Next we use this expansion to obtain the expansion of the matrix operators $C_{nn'}$ in eqn. (2.4) and we also expand V_{ion} in powers of κ. The final step is then to solve eqn. (2.4) by a perturbation expansion in κ; thereby obtaining an expansion for the exact eigenvalue $\mathscr{E}$:

$$\mathscr{E}_m=\sum_s \kappa^s\mathscr{E}_m^{(s)} \qquad (3.76)$$

and wave function

$$\Phi_m=\sum_s \kappa^s\Phi_m^{(s)}. \qquad (3.77)$$

We find that

$$\mathscr{E}_m^{(0)}=E_m^{(0)}; \qquad \mathscr{E}_m^{(1)}=0. \qquad (3.78)$$

The second-order term $\mathscr{E}_m^{(2)}$ is the eigenvalue of the harmonic approximation equation:

$$(T_{\text{ion}}+V_{\text{ion}}^{(2)}+E_n^{(2)})\chi_{mn}^{(0)}=\mathscr{E}_m^{(2)}\chi_{mn}^{(0)}. \quad . \quad . \quad (3.79)$$

As we have already mentioned, the whole difficulty in this procedure stems from the fact that we have in fact to solve eqn. (2.1) for the motion of the electrons in the presence of the fixed ions and interacting with each other via their mutual Coulomb interactions. The simplest approximation to this problem which retains some (at least) of the essential features is provided by the Hartree–Fock approximation. The only difference between eqn. (2.1) and the familiar many-electron equation is that it contains an extra interaction energy between each electron and the fixed ions. This extra interaction energy is a sum of single electron terms and the Hartree–Fock equations for this problem merely have an extra potential energy term in them arising from this interaction. If we set up the variational equation using a Slater determinant of single particle wave functions $\phi_{\mathbf{k}}(\mathbf{r}|\mathbf{R})$ which are allowed to depend parametrically on the coordinates R of the ions we find that they must satisfy the equation

$$\mathscr{H}_0\phi_{\mathbf{k}}+V_{\text{int}}(\mathbf{r}|\mathbf{R})\phi_{\mathbf{k}}=\epsilon_{\mathbf{k}}\phi_{\mathbf{k}}, \quad . \quad . \quad . \quad . \quad . \quad (3.80)$$

where

$$\mathscr{H}_0\phi_{\mathbf{k}}=-\frac{\hbar^2}{2m}\nabla^2\phi_{\mathbf{k}}-\sum_{\substack{\mathbf{k}'\\ \|\text{ Spins}}}V_{\mathbf{kk}'}{}^{C}\phi_{\mathbf{k}'} \quad . \quad . \quad . \quad (3.81)$$

and is the usual Hartree Fock Hamiltonian; $V_{\text{int}}(\mathbf{r}|\mathbf{R})$ is the interaction energy between one electron and the entire array of ions in an arbitrary configuration $\mathbf{R}_1, \mathbf{R}_2 \ldots \mathbf{R}_N$. We have therefore reduced the many-body eigenvalue (eqn. (2.1)) to a simple Hartree–Fock equation for the single particle function $\phi_{\mathbf{k}}(\mathbf{r}|\mathbf{R})$. We now solve eqn. (3.80) by a series expansion in κ; we write

$$\phi_{\mathbf{k}}=\phi_{\mathbf{k}}{}^0+\sum_{n\geqslant 1}\sum_{\mathbf{k}'}\kappa^n b_{\mathbf{kk}'}{}^{(n)}\phi_{\mathbf{k}'} \quad . \quad . \quad . \quad (3.82)$$

and

$$\epsilon_{\mathbf{k}}=\epsilon_{\mathbf{k}}{}^0+\sum_{n>1}\kappa^n\epsilon_{\mathbf{k}}{}^{(n)}.$$

Here $\phi_{\mathbf{k}}{}^0$ satisfies the equation

$$(\mathscr{H}_0+V_{\text{int}}{}^{(0)})\phi_{\mathbf{k}}{}^0=\epsilon_{\mathbf{k}}{}^0\phi_{\mathbf{k}}{}^0 \quad . \quad . \quad . \quad . \quad (3.83)$$

and is of course a plane wave solution with eigenvalue

$$\epsilon_{\mathbf{k}}{}^{(0)}=E_{\mathbf{k}}=\epsilon_{\mathbf{k}}-W_{\mathbf{k}}. \quad . \quad . \quad . \quad . \quad . \quad (3.84)$$

Here $\epsilon_{\mathbf{k}}$ is the usual Bloch energy of an electron moving in the static potential $V^{(0)}(\mathbf{r}|\mathbf{R}_0)$, and $W_{\mathbf{k}}$ is the exchange energy.

To calculate the frequencies of the lattice in this scheme we require

$$E_n{}^{(2)}=\sum_{\mathbf{k}}n(\mathbf{k})\epsilon_{\mathbf{k}}{}^{(2)}\kappa^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.85)$$

The $n(\mathbf{k})$'s are the usual unperturbed occupation numbers

$$\left.\begin{array}{ll} n(\mathbf{k})=1 & |k|<k_{\mathrm{F}}, \\ n(\mathbf{k})=0 & |k|\geqslant k_{\mathrm{F}}. \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (3.86)$$

To calculate $\epsilon_{\mathbf{k}}^{(2)}$ we need $\phi_{\mathbf{k}}$ to first order in κ; we find that

$$\epsilon_{\mathbf{k}}^{(2)}=2\sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'}^{(1)} b_{\mathbf{k}\mathbf{k}'}^{(1)} q_{\mathbf{k}-\mathbf{k}'}. \quad . \quad . \quad . \quad . \quad . \qquad (3.87)$$

If we set $\mathbf{k}'=\mathbf{k}+\mathbf{f}$ and write

$$b_{\mathbf{k}\mathbf{k}'}^{(1)}=b_{\mathbf{k},\,\mathbf{f}}^{(1)}=\frac{v(\mathbf{k},\mathbf{f})q_{\mathbf{f}}}{E_{\mathbf{k}}-E_{\mathbf{k}-\mathbf{f}}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.88)$$

then the first-order approximation to eqn. (3.81) can be written as:

$$v(\mathbf{k},\mathbf{f})=V_{\mathbf{f}}^{(1)}+\sum_{\mathbf{k}'}\frac{n(\mathbf{k}')(V_{\mathbf{f}}^{\mathrm{C}}-V_{\mathbf{k}-\mathbf{k}'}^{\mathrm{C}}-V_{\mathbf{k}-\mathbf{k}'-\mathbf{f}}^{\mathrm{C}})v(\mathbf{k}',\mathbf{f})}{(E_{\mathbf{k}'-\mathbf{f}}-E_{\mathbf{k}'})} \quad . \quad . \qquad (3.89)$$

This is identical, apart from the definition of the $n(\mathbf{k})$'s, with eqn. (3.34). If the exchange energy $W_{\mathbf{k}}$ and the terms containing the factors $V_{\mathbf{k}-\mathbf{k}'}^{\mathrm{C}}$ and $V_{\mathbf{k}-\mathbf{k}'-\mathbf{f}}^{\mathrm{C}}$ are neglected this equation becomes identical with that used by Bardeen (1937). We then find that

$$E_{n}^{(2)}=-\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{f}}\frac{v(\mathbf{k},\mathbf{f})V_{-\mathbf{f}}^{(1)}n(\mathbf{k})}{(E_{\mathbf{k}}-E_{\mathbf{k}-\mathbf{f}})}q_{\mathbf{f}}q_{\mathbf{f}}^{*}, \quad . \quad . \quad . \quad . \qquad (3.90)$$

and lattice frequencies $\omega_{\mathbf{f}}$ are given by the equation

$$\omega_{\mathbf{f}}^{2}=\Omega_{\mathbf{f}}^{2}-V_{-\mathbf{f}}^{(1)}\sum_{\mathbf{k}}\frac{v(\mathbf{k},\mathbf{f})n(\mathbf{k})}{E_{\mathbf{k}}-E_{\mathbf{k}-\mathbf{f}}}. \quad . \quad . \quad . \quad . \quad . \qquad (3.91)$$

The only difference between these equations and the results we found in §3.3 is that the sums over occupation numbers are now over the usual unperturbed Fermi distribution (3.86).

The lowest order one-phonon interaction term that can lead to real transitions is now given by the lowest order term in $A_{nn'}$: this is

$$A_{nn'}^{(3)}=-\frac{\hbar^{2}}{2m}\int\psi_{n}^{0}\nabla_{\mathbf{R}_j}\psi_{n}^{(1)}\,d\tau\,\nabla_{\mathbf{R}_j}. \quad . \quad . \quad . \quad . \quad . \qquad (3.92)$$

If we introduce normal coordinates and momenta for the lattice degrees of freedom and express $\psi_{n}^{(1)}$ in terms of $v(\mathbf{k},\mathbf{f})$, eqn. (3.88), we find that $A_{nn'}^{(3)}$ has the form

$$\sum_{\mathbf{k},\mathbf{f}}\frac{v(\mathbf{k},\mathbf{f})}{E_{\mathbf{k}}-E_{\mathbf{k}-\mathbf{f}}}\dot{p}_{\mathbf{f}}a_{\mathbf{k}}^{*}a_{\mathbf{k}-\mathbf{f}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.93)$$

This differs from the expression given in eqn. (3.59) in that the energy denominator has the Hartree Fock energies $E_{\mathbf{k}}$ rather than the Bloch energies $\epsilon_{\mathbf{k}}$. On the energy shell it is of order κ.

It is clear that by proceeding in this way we can calculate the Hartree-Fock approximation to every term in the Born Oppenheimer expansion. The method therefore has the same limitations as the expansion itself.

§ 4. THERMODYNAMIC FUNCTIONS AND TRANSPORT COEFFICIENTS

4.1. *Thermodynamic Functions*

In this section we shall discuss the influence of electron–phonon interactions on the equilibrium properties of a metal. We first consider two properties, the cohesive energy and the normal mode frequencies that we believe are not very sensitive to electrons in the 'danger zone'. The cohesive energy or, what is essentially the same thing, the ground state energy of the system can be written as

$$\mathscr{E}_0 = E_0 + \sum \tfrac{1}{2}\hbar\omega_{\mathbf{f}} + \Delta E, \qquad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where E_0 is the lowest electronic eigenvalue for the static lattice problem. $\sum \frac{1}{2}\hbar\omega_{\mathbf{f}}$ is the zero point energy of the lattice vibrations and ΔE is the correction term that we are interested in. This expression is correct no matter which of the methods we use; there is only a small difference in the definition of the frequencies in the various methods. In Nakajima's method the lowest approximation to ΔE is

$$\Delta E = \Delta E_N = \sum \frac{n_{\mathbf{k}}(1-n_{\mathbf{k}-\mathbf{f}})|V_{\mathbf{f}}|^2}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}})^2-(\hbar\omega_{\mathbf{f}})^2}. \qquad . \quad . \quad . \quad . \quad (4.2)$$

while in the Born–Oppenheimer and Hartree–Fock methods the lowest approximation gives

$$\Delta E = \Delta E_B = \sum \frac{n_{\mathbf{k}}(1-n_{\mathbf{k}-\mathbf{f}})|V_{\mathbf{f}}|^2}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}})^2}, \qquad . \quad . \quad . \quad . \quad (4.3)$$

Both the expressions contain formally divergent sums due to vanishing energy denominators. We have seen that a possible description for such sums in the Nakajima method is to define them by taking a principal part. If this is done then we in fact find that $\Delta E_N \sim (m/M)^{1/2}\sum_{\mathbf{f}}\frac{1}{2}\hbar\omega_{\mathbf{f}}$ and is very small indeed. The divergent sum in eqn. (4.3) can be defined by taking principal parts—though we do not now have a very good reason for doing so. If the sum is defined in this way then we again find that

$$\Delta E_B \sim (m/M)^{1/2} \sum_{\mathbf{f}} \tfrac{1}{2}\hbar\omega_{\mathbf{f}}.$$

Thus both ΔE_N and ΔE_B are about 10^{-4} ev in magnitude. While this is of course far beyond the accuracy with which we can hope to calculate E_0, it is very large indeed compared with the energy difference between the normal and superconducting states of a metal which is of the order of 10^{-7} ev. We mention this at this point to emphasize the enormous difficulty that would arise if we were to attempt to calculate these small energy differences from first principles. The divergences that arise in eqns. (4.2) and (4.3) of course come entirely from electrons in the danger zone. We could in fact argue that even though the methods cannot treat these electrons properly it is very unlikely that they contribute a larger amount to $\mathscr{E}_0$ than all the rest of the electrons do. Consequently our numerical estimate of ΔE is likely to be reliable. If this is so then we can conclude that it is in fact quite negligible.

We have already given formulae for the normal mode frequencies eqn. (3.44); we shall work in the framework of the simple Hartree approximation, eqn. (3.37). This leads to the following expression for the velocity of sound

$$c_s = \left(\frac{N}{M}\right)^{1/2} \frac{1}{\sqrt{S_0}}, \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.4)$$

where S_0 is defined by the equation

$$S_0 = \lim_{|\mathbf{f}|\to 0} \sum_{\mathbf{k}} \frac{n(\mathbf{k})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}} - \omega_{\mathbf{f}}} + \sum_{\mathbf{k}} \frac{n(\mathbf{k})}{\epsilon_{\mathbf{k}} - {}_{\mathbf{k}-\mathbf{f}}\epsilon + \omega_{\mathbf{f}}}. \qquad . \quad . \quad (4.5)$$

In the Hartree-Fock method the phonon energy $\omega_{\mathbf{f}}$ would be absent in the denominator. This leads to a very small difference in the velocity of sound in the two methods; see Appendix 3. We can therefore write

$$\begin{aligned} S_0 &= \lim_{|\mathbf{f}|\to 0} 2\sum \frac{n(\mathbf{k})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}} \\ &= \lim_{|\mathbf{f}|\to 0} \sum \frac{n(\mathbf{k}) - n(\mathbf{k}-\mathbf{f})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}}. \qquad . \quad . \quad . \quad . \quad (4.6) \end{aligned}$$

This last expression for S_0 shows that it is only dependence on these terms in the sum for which $\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}-\mathbf{f}}$ lie very close to the Fermi surface, and are in fact in the danger zone. On the other hand the general expression given by eqn. (3.44) for the normal mode frequencies shows that for most values of $|\mathbf{f}|$ the important terms in the sum for $S(\mathbf{f})$ come from electrons lying well away from the Fermi surface. We conclude that the normal mode frequencies are sensitive to electrons in the danger zone for small wave numbers. For large wave numbers they are not. For a spherical Fermi surface we can write

$$S_0 = \lim_{|\mathbf{f}|\to 0} \sum_{\mathbf{k}} \frac{n(\mathbf{k}) - n(\mathbf{k}-\mathbf{f})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}} = N(E_{\mathrm{F}}), \qquad . \quad . \quad . \quad . \quad (4.7)$$

where $N(E_{\mathrm{F}})$ is the density of states at the Fermi surface. This expression for S_0 leads to the simple formula for the velocity of sound given by eqn. (3.39). The fact that this simple calculation leads to results of the correct order of magnitude encourages one to believe that in this instance we may have given a reasonably accurate description of the motions of the electrons in the danger zone. A more sophisticated comparison of the normal mode frequencies with experiment has been carried out by Bardeen and Pines (1955). They conclude that the elastic constants calculated from the frequencies agree with the experimental values in the alkali metals to within about 20%.

It has been pointed out by Kohn (1960) that the equation for omission implies that $\partial\omega(\mathbf{f})/\partial|\mathbf{f}|$ has singularities at certain values of $|\mathbf{f}|$, for a free electron model we find that

$$\begin{aligned} \partial\omega/\partial|\mathbf{f}| &= -\tfrac{1}{2}\omega_{\mathbf{f}}^2/\Omega_{\mathbf{f}} V_{\mathbf{f}}^{\mathrm{C}}\, \partial S(\mathbf{f}) \frac{\partial S(\mathbf{f})}{\partial|\mathbf{f}|} \\ &= -\tfrac{1}{2}\omega_s^2/\Omega_{\mathbf{f}} V_{\mathbf{f}}^{\mathrm{C}} \frac{3N}{4E_{\mathrm{F}}}\left[\frac{1}{|\mathbf{f}|} - \frac{4k_{\mathrm{F}}^2 + |\mathbf{f}|^2}{4k_{\mathrm{F}}|\mathbf{f}|^2} \log\left|\frac{2k_{\mathrm{F}} + |\mathbf{f}|}{2k_{\mathrm{F}} - |\mathbf{f}|}\right|\right] \qquad (4.8) \end{aligned}$$

and hence has a logarithmic singularity at $|\mathbf{f}| = 2k_{\mathrm{F}}$.

If a more general expression for the single particle energies is used then Kohn has shown that the singularities in $\partial\omega(\mathbf{f})/\partial|\mathbf{f}|$ can give information about the shape of the Fermi surface. These singularities have recently been detected in lead by Brockhouse (1961). The most prominent of them does occur at $|\mathbf{f}|=2k_{\mathrm{F}}$. Lead is probably an especially favourable case because the 'magnitude' of the singularity clearly depends on the size of the matrix element and this is known to be large in lead.

We now turn to two quantities that may be very sensitive to electrons near the Fermi surface; namely the specific heat and the spin paramagnetism. The lowest order corrections to the specific heat can be calculated quite easily by treating the correction terms, eqn. (3.45), by perturbation theory. If we calculate the lowest order correction F^{C} to the free energy in Nakajima's method, then we arrive at the same expression as Buckingham and Schafroth (1954), namely

$$F^{\mathrm{C}}=\sum\frac{\bar{n}_{\mathbf{k}}(1-\bar{n}_{\mathbf{k}-\mathbf{f}})v_{\mathbf{f}}^2}{|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}|^2-(\hbar\omega_{\mathbf{f}})^2}. \qquad (4.9)$$

Now F^{C} is temperature dependent through the Fermi functions $\bar{n}_{\mathbf{k}}$ in the numerator of the sum in eqn. (4.9). These imply that the temperature dependent part of the product $\bar{n}_{\mathbf{k}}(1-\bar{n}_{\mathbf{k}-\mathbf{f}})$ will be non-zero for transitions for which $\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}-\mathbf{f}}$ lie within kT of the Fermi surface. A rough estimate of the magnitude of the energy denominator for these transitions is $(kT)^2-(\hbar\omega)^2$, where $\bar{\omega}$ is an average value of $\bar{\omega}$. At temperatures such that $kT\leqslant h\bar{\omega}$ we can therefore approximate F^{C} as *far as its temperature dependence is concerned* by the expression

$$F^{\mathrm{C}}\simeq\sum_{\mathbf{k}}\frac{\bar{n}_{\mathbf{k}}(1-\bar{n}_{\mathbf{k}-\mathbf{f}})}{(\hbar\bar{\omega})^2}|v_{\mathbf{f}}|^2. \qquad (4.10)$$

It is clear that this term can be quite large because of the very small energy denominator. In fact a simple order of magnitude estimate of (4.10) indicates that it is of order $C(kT/E_{\mathrm{F}})^2$, where C is the conventional (Wilson 1953) electron-phonon coupling constant. Since C ranges in value from $(\frac{1}{8}-1)E_{\mathrm{F}}$ it is clear that the correction to the temperature dependent part of F^{C} is quite comparable with the ordinary temperature dependent part of the unperturbed free energy which is of order of magnitude $E_{\mathrm{F}}(kT/E_{\mathrm{F}})^2$. A detailed calculation of the specific heat contribution from F^{C} has been made by Buckingham and Schafroth (1954). They find that at low temperatures the specific heat has an extra term

$$\delta c=\gamma_S T\left(\frac{3C}{4E}\right)^2\left(\frac{1}{2}\right)^{1/3} \qquad (4.11)$$

where $\gamma_S T$ is the usual Sommerfeld specific heat. At temperatures above the Debye temperature we can no longer argue that $\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}$ is very small compared with the average value of $h\omega_{\mathbf{f}}$. The energy denominator will now be quite large on the average and we must expect that the extra contribution to the specific heat will be greatly reduced. This expectation is confirmed by the calculations of Buckingham and Schafroth who find that for $T \geqslant \theta$ the contribution (4.11) is reduced by a factor $k\theta/E_{\mathrm{F}} \sim 10^{-2}$ and is consequently quite negligible. It is clear from this discussion that the very large contribution to the specific heat came from transitions in the region of the Fermi distribution that is thermally excited. That is a region of width kT about E_{F}; consequently if kT is small we are led to very small energy denominators. The importance of this result lies in the fact that the effect comes entirely from electrons near the Fermi surface. If therefore it were possible to check it experimentally, then we should have a direct check on the validity of the method for this group of electrons. So far no experimental check has proved possible—one should note that C is independent of the mass M of the ions and so there is no dependence of δc on M. There are of course small corrections to the specific heat from the dependence of the normal mode frequencies on the distribution of electrons. These corrections have been calculated by Chester and Houghton (1959) who find that they amount to only a few per cent.

The effect of the correction terms to the free energy in the spin susceptibility can also be computed. This is perhaps of more interest as it is possible to measure the susceptibility over a wide range of temperatures. In contrast the 'electronic' specific heat of a metal is only directly observable at low temperatures when the lattice specific heat is negligible.

In Appendix 2 we outline the calculation. We find a correction $\delta\chi_0$ to the temperature independent susceptibility χ_0, given by,

$$\delta\chi_0 \sim \mathrm{O}\left(\frac{k\theta}{E_{\mathrm{F}}}\right)\chi_0; \qquad \ldots \ldots \ldots \quad (4.12)$$

whereas the temperature dependent part χ_T has a correction

$$\left.\begin{aligned} \delta\chi_T &\sim \mathrm{O}(C)\chi_T & &(T \leqslant \theta), \\ &\sim \mathrm{O}\left(\frac{k\theta}{E_{\mathrm{F}}}\right)\chi_T & &(T \geqslant \theta), \end{aligned}\right\} \quad \ldots \ldots \quad (4.13)$$

where C is again the electron phonon coupling constant. These results are really very similar to those we found for the free energy. There the temperature independent part—the ground-stage energy—had a negligible correction while the temperature dependent part had a correction of exactly the same form as χ_T. The most important conclusion to be drawn from this result for χ is that the effects of the electron phonon correction terms cannot be simply described in terms of a modified density of states for the electrons. For if this were so we must expect that χ and C would be modified in the same way. The physical reason for the small modification of χ_0 appears to be that the distortion of the Fermi distribution caused by the application of a magnetic field is really quite different from that caused by raising the temperature of the metal. For in the latter case electrons are excited above the Fermi level and holes are left below; consequently transitions can take place quite freely among states within kT of E_F. When a magnetic field is applied electrons of one spin orientation are 'excited' to states above E_F and electrons of the opposite spin orientation are 'removed' to states below E_F. One if therefore tempted to say that a certain number of 'electron-hole' pairs have been created. This is not really correct however because all the excited electrons have one spin orientation and all the holes, the opposite. Since the electron–phonon interaction cannot change the spin of an electron *no* transitions are possible between the 'electrons' and 'holes' and χ_0 is not appreciably modified by the electron–phonon interaction. Again there are other small corrections to χ_0 from the normal mode frequencies. They amount to only a few per cent (Chester and Houghton 1959). It should perhaps be mentioned that they are temperature dependent; so a very accurate measurement might detect their presence. No direct calculation of the effects of electron–phonon interactions on the Knight shift have been made. We have little doubt that qualitatively the results will be very similar to those we have described for the spin susceptibility.

It should be clear from this discussion that while many properties of a metal are really quite insensitive to the behaviour of the electrons near the Fermi sea, there are others which are really very sensitive indeed to the way we deal with those electrons. Any experiments that would give information about this very special group of electrons would be extremely valuable.

In conclusion we should like to mention that it is likely that for $T > \theta$ an entirely different approach to the problems we have just discussed can be found. For at such temperatures it is plausible that we can expand the partition function in powers of θ/T. Since $\theta \propto M^{-1/2}$ this would be an expansion in powers of κ^2 and would be closely related to the Born–Oppenheimer expansion. However, we suspect that it might have a wider range of validity than that expansion. The reason for this is that in the expansion of the partition function we would only require that $\zeta/kT < 1$ rather than that $\zeta/\Delta E < 1$, where ζ is a measure of the strength of the 'perturbation' we are considering. In our case $\bar{C}$ would be the average value of the non-adiabatic terms $C_{nn'}$ in the equations of motion. The energy difference ΔE is the energy separation of the states we are interested in. Now we saw that we could satisfy the criterion $\bar{C}/\Delta E < 1$ except possibly for a group of states very close to E_F for which ΔE is very small. However, if this criterion is replaced by $\bar{C}/kT$ then this particular group of states no longer plays any special role. This is an example of a familiar situation in statistical mechanics. The difficulties that arise in Rayleigh–Schrödinger perturbation theory due to small energy denominators do not occur in the perturbation expansion of the free energy at a finite temperature (Schrafroth 1951). If we use our estimate of $C_{nn'}$ then we require that

$$\frac{\hbar\bar{v}}{lkT} < 1.$$

Now v is close in magnitude to the velocity of sound, and $l^{-1} \sim a^{-1}$ where a is the interatomic spacing. Consequently $\hbar \bar{v} l^{-1} \sim \hbar c a^{-1} \sim \hbar \omega_{\max} \sim k\theta$, and we then require that

$$\theta/T < 1$$

as we guessed earlier. The low-order terms in this expansion have recently been obtained (Major 1960, unpublished) and the expansion appears to converge well for $T > \theta$.

4.2. *Transport Coffiecients*

In § 3 we have discussed in detail how the various theoretical approaches handle the real one-phonon processes that we believe are responsible for the electrical and thermal resistance of a metal. Our conclusions in that section were (*a*) that the Nakajima method can be modified to handle these processes in a satisfactory manner, (*b*) the Born–Oppenheimer and Hartree–Fock methods lead directly to interaction terms in the Hamiltonian which give rise to this type of transition. We showed in fact that in all three methods the interaction term on the energy shell could be written in the form

$$\sum_{\mathbf{k},\mathbf{f}} \frac{p_{\mathbf{f}}}{\omega \hbar_{\mathbf{f}}} a_{\mathbf{k}}{}^{*} a_{\mathbf{k}-\mathbf{f}} v(\mathbf{k}, \mathbf{f}). \qquad \dots\dots \qquad (4.14)$$

Since the matrix elements of $p_{\mathbf{f}}/\hbar\omega_{\mathbf{f}}$ are the same as those of $q_{\mathbf{f}}$ this interaction term is very similar to the one that is introduced phenomenologically in the theory of transport coefficients (Wilson 1953). The only difference being that the effective matrix element $v(\mathbf{k}, \mathbf{f})$ depends on the wave vector $\mathbf{k}$ as well as on the difference of wave vectors between the initial and final states. If we make the simple Hartree approximation the $v(\mathbf{k}, \mathbf{f})$ is replaced by Bardeen's (1937) matrix element $v(\mathbf{f})$. A detailed discussion of this matrix element has been given by Ziman (1960). In § 3 we referred to two attempts by Hone (1960) and Bailyn (1960) to compute $v(\mathbf{k}, \mathbf{f})$ from the more general eqn. (3.42). They both compute averages of $v(\mathbf{k}, \mathbf{f})$ over all values of $\mathbf{k}$. These average values turn out to be comparable in magnitude in $v(\mathbf{f})$. The eqn. (3.42) is a three-dimensional integral equation in which one of the variables (the azimuthal angle) can be disposed of. There would probably be little difficulty in solving it numerically. It would of course be very difficult to use the computed matrix element to calculate the transport coefficients. Nevertheless it would be of considerable interest to compare $v(\mathbf{k}, \mathbf{f})$ with the much simpler Bardeen matrix element $v(\mathbf{f})$. At this stage we should point out that the calculation of both $v(\mathbf{f})$ and $v(\mathbf{k}, \mathbf{f})$ becomes very much more difficult if we start to consider the detailed band structure of the metal; results can only really be obtaiend for very simple models (Ziman 1961). The qualitative agreement with experiment when the simple Bardeen matrix element is used is quite good; this gives us some confidence in the basic methods employed. The thermoelectric power of a metal does seem (Ziman 1960) to be very sensitive to the 'shape' of the matrix element and this property may therefore provide some additional information about the assumptions on which the theory is based.

We conclude this section by pointing out that the effect of the diagonal self-energy terms in eqn. (3.45) on the transport coefficients has never been investigated. Since the electrons involved in the transport of energy and charge are again those very near to the Fermi surface these self-energy terms might give a significant modification to some of the transport coefficients. Perhaps the simplest quantities to consider in this connection are the anomalous skin effect (in the extreme anomalous limit) and the Wiedemann–Franz ratio.

§ 5. SUPERCONDUCTIVITY

The superconducting transition temperatures of mercury (Maxwell 1950 a), tin (Maxwell 1950 b), lead (Olsen-Bör 1951) and thallium (Maxwell 1951), depend on the mass of the ions in the lattice. The transition from the normal to superconducting state of these metals must therefore be influenced by the interactions of the electrons with the vibrating lattice. Quite independently of these experiments Fröhlich (1950) suggested that the exchange of virtual phonons by the electrons could lower the energy of a metal and cause a transition of the superconducting state. It is tempting to generalize from the rather scanty data we have mentioned and to say that the transition temperatures of all superconductors will depend upon the mass M of the ions in the lattice. However it has recently been shown (Geballe *et al.* 1961) that the transition temperature T_c of ruthenium has at most only a very weak dependence on M. For the four elements we have mentioned earlier $T_c \propto M^{-1/2}$; T_c for ruthenium shows less than 10% of the variation that would follow from this dependence. The most that can therefore be said with certainty at the present time is that the electron–phonon interaction plays some part in the transition to the superconducting state. It is by no means established that it plays any very general role. What is obviously required are more extensive measurements on a much wider range of metals to see to what extent the dependence of T_c on the isotopic constitution is a general phenomenon.

We do not intend to review the current theories of superconductivity (Bardeen *et al.* 1957, Bogolyubov *et al.* 1959) in detail. The reason being that the current theories only require that there be some effective interaction between the electrons which is attractive close to the Fermi energy. The theories are not sufficiently well developed to determine whether this interaction must come via the phonons or could arise from another source. One can in fact legitimately regard the theories as models of the superconducting state in which it is postulated that an attractive interaction exists between electrons with energies close to the Fermi energy. The importance of this type of attractive interaction was first realized by Cooper (1956). He showed that if *two electrons* moving above a Fermi sea of non-interacting electrons had an attractive interaction then they could form a 'correlated state' with an energy lower than the Fermi energy of the system. The motion of the two electrons in this state is correlated over very large distances (of the order 10^{-4} cm) and there is an energy gap in the spectrum of the excited states of the system. It is now believed (Van Hove 1959) that it is a quite general feature of Fermi systems that the normal state, in which the electrons are pictured as filling a Fermi distribution up to a definite level, becomes unstable in the presence of an attractive interaction. We say 'believed' because there is no general theoretical proof of this assertion. If this is the case then we are immediately faced with the problem of explaining why only some (40%) of the metallic elements are superconductors. This is of course an extremely difficult question to answer. The usual reason put forward is that the Coulomb (screened or otherwise) interaction is certainly repulsive and must to some extent balance out any other attractive interaction.

There is one other point that is worth discussing qualitatively. This is whether it is possible to decide which, if any, particular group of electrons is involved in the transition from normal to superconducting state. There are quite strong arguments to support the view that only a small fraction of all the electrons in the metal are appreciably affected by the transition. The strongest argument being the very small energy difference between the two states. This energy difference is typically about 1 part in 10^{-8}. If all the electrons were involved in the transition this would imply a change of energy of about 10^{-7} ev per electron. While such a very small energy change for all the electrons cannot be ruled out it seems much more plausible to assume that a much smaller number is involved and that each suffers a comparatively large energy change. Now we have already given a qualitative argument (§2) that the bulk of the electrons probably follow the motion of the lattice in a simple adiabatic fashion. We estimated that only those electrons within $\hbar\omega_{\max}$ of the Fermi energy are likely to be affected in a non-adiabatic way by the motion of the lattice. If only these electrons were involved in the transition then the energy change per electron would be about $E_{\mathrm{F}}/\hbar\omega_{\max} \times 10^{-7}$ ev $\sim 10^{-4}$ ev. Since this is of the order of kT_c where T_c is the transition temperature it seems to be a much more reasonable quantity than 10^{-7} ev. We believe that the qualitative argument we gave in §2 does lend some support to the view that it is in fact electrons in this special region that are involved in the transition.

If this conclusion is correct, then we can understand at once why quantities used as the cohesive energy, normal mode frequencies and the effective matrix element v_{f} are changed very little by the transition. For all of these quantities involve all the electrons in the Fermi distribution and only a small fraction ($\hbar\omega_{\max}/E_{\mathrm{F}}$) of these are involved in the transition. On the other hand the specific heat, and spin susceptibility should be considerably modified as these involve electrons in the region within

$\hbar\omega_{\max}$ of E_F. It is of course quantities just like these that are found experimentally to be quite different in the two states.

We must now consider whether any of the methods that have been described in § 3 could provide a satisfactory basis for a theory of superconductivity. As we have seen, what is probably required is an interaction between the electrons which is attractive in the neighbourhood of the Fermi energy. Unfortunately it is just in this region of energies that the theories are least reliable. Examination of eqns. (3.27), (3.65), which define the transformations S^N and S^B, shows at once that they become large when $|\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}| < \hbar\omega_{\max}$. One cannot have much faith in the convergence of the perturbation expansions for these electrons. This point has been made more precisely by Bardeen (1956).

In spite of this fact Bardeen *et al.* (1957) did attempt to base their original theory on the effective interaction derived by Nakajima (1953). This interaction, eqn. (3.45), becomes large and negative for transitions in which $|\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{f}}| < \hbar\omega_{\max}$. In their original paper Bardeen *et al.* assumed that this was the most important part of the interaction and used it to develop the theory. However, since none of the *detailed* properties of the interaction was used in the subsequent development it is really left quite open whether this particular form of the interaction is vital to the theory. In other words only the more detailed quantitative features of the behaviour of superconductors can help us to determine the structure of the interaction terms in the Hamiltonian. The only attempt that has been made to correlate the interaction with experimental properties of superconductors is due to Pines (1958) and Morel (1959).

Bogolyubov (1957) started from the usual phenomenological screened interaction (Fröhlich 1950, Wilson 1953). As we have seen, there is very little justification for introducing such an interaction except for real one-phonon processes. Indeed if this interaction is introduced then it is very difficult to introduce Coulomb forces between the electrons and treat them consistently; for a ‘large part’ of these forces has already been taken into account in the screened interaction. It is in fact quite easy to make the mistake of screening the electron–phonon interaction ‘twice over’. As far as we are able to see the later work by Bogolyubov *et al.* (1959) on the Coulomb effects does contain this error. However, if his basic Hamiltonian is ‘reinterpreted’ in terms of bare rather than screened interactions, then his final results (eqn. (6.28), Chapter 6) for the renormalized frequencies and matrix element are identical with those we derived using the Hartree approximation. For this reason we do not think that his method of handling the electron–phonon interaction is any more convincing that that of Bardeen *et al.*

We conclude this section with some suggestions about how the current methods could be modified to provide a satisfactory basis for a theory of superconductivity. The major defect of the methods we have described is that they are all in some sense ‘perturbative’. This is clear from the fact that the final physical properties are expressed in terms of the Bloch (or exchange) energies of the electrons. In particular the effective electron–electron interaction term contains these energies in the denominator. Now if we believe that the excitation spectrum of a superconductor is quite different from the Bloch energy spectrum, then we might expect that the actual energies of the excitations should appear in such quantities as the velocity of sound or the electron–phonon matrix element. However, the excitation spectrum of a superconductor is not the solution of any naive zero-order approximation. This suggests that a satisfactory theory can only be developed if the zero-order approximation is correctly chosen. A possible way of choosing the zero-order approximation would be to suppose that there is an attractive interaction between the electrons and to add and subtract this from the Hamiltonian. The zero-order approximation could be chosen to include this attractive interaction and we would then obtain a superconducting state as the solution to the lowest order equations. If now a canonical transformation similar to Nakajima's is applied to the Hamiltonian, then the frequencies would be renormalized in terms of the excitation spectrum of the superconducting state. The attractive interaction that we have also subtracted from the Hamiltonain could be eliminted in a self-consistent manner by demanding that it be cancelled by the interaction term (eqn. (3.45)) that is generated by the canonical transformation. If a programme like this could be carried through, the physical quantities such as the frequencies and effective matrix elements would be expressed in terms of the actual excitation spectrum of the system. This would in turn imply that the energy denominators would never vanish if there is a gap in the excitation spectrum. An alternative scheme would be to transform the Hamiltonian in terms of quasi-particle operators (Valatin 1958, Bogolyubov *et al.* 1959) before attempting to renormalize the bare frequencies and matrix element for the electron–phonon interaction. This is essentially the method used by Bogolyubov in his original treatment of the problem—except that he started with a screened electron–phonon interaction and omitted the Coulomb terms. As we have already mentioned one can 'reinterpret' his basic Hamiltonian in terms of bare interactions rather than screened ones. If this is done then the renormalized frequencies and matrix elements are indeed expressed in terms of the actual excitation energies of the system. This method does of course lead to a complicated set of equations that have to be solved self-consistently. So far only the simplest approximations have been made to this problem. These lead to the usual Hartree approximation (§ 3.4) to the matrix elements and frequencies.

We conclude this section with some comments on the low-temperature specific heat of superconductors. It has recently been found (Bryant and Keesom 1960, Borse *et al.* 1960) that at very low temperatures $T/T_c \leqslant 1/7$, the specific heat of superconducting niobium and indium does not tend towards the lattice specific heat of the normal state but to a value lower than this. The data can be fitted to a T^3 curve which we can write in the form

$$C_s = A_n T^3 - BT^3 \qquad (T/T_c \leqslant 1/7), \quad . \quad . \quad . \quad . \quad (5.1)$$

where the term $A_n T^3$ is the normal lattice specific heat. The term $-BT^3$ is about 10–15% of this at the temperatures of interest. The 'constant' B may be temperature dependent, Bryant and Keesom suggest that $B \sim e^{-1\cdot 9/T}$. It would seem that both terms in eqn. (5.1) could be combined into a single term and one could then say that the lattice specific heat has altered by some 10%. This would imply a change in the velocity of sound of about 3%. Direct measurements by Chandrasekhar and Rayne (1961) show that the velocity of sound in indium changes by only 1 part in 10^{-5}, so that this simple suggestion cannot be correct. An alternative suggestion has been put forward by Daunt and Olsen (1961). They point out that the free energy of the system always contains the 'zero-point energy' of the lattice modes $\sum_{\mathbf{f}} \frac{1}{2}\hbar\omega_{\mathbf{f}}$. Now we have seen that the frequencies $\omega(\mathbf{f}, s)$ depend on the electronic configuration through the presence of the factor $n(k)$ in eqn. (3.35). In §4.2 we pointed out that because of this there is a contribution to the specific heat of a few per cent in the normal state of a metal. Daunt and Olsen suggest that a similar effect should arise in the superconducting state and would lead to an additional term in the specific heat. This term really arises because of the coupling between the motion of the ions and electrons. It is not therefore a contribution arising from an additional mode of motion that has been neglected—for this reason it can have a negative sign. No actual calculation of the size or sign of this contribution has been published. The effect certainly exists and the calculation is perfectly straightforward. It is perhaps rather strange to talk in terms of a temperature dependent zero-point energy. One normally talks in terms of a zero-point energy that is associated with the ground state of the entire metal. However, since the frequencies $\omega(\mathbf{f}, s)$ depend on the electronic state of the system the 'zero-point energy' $\frac{1}{2}\hbar\omega_{\mathbf{f}}$ will also depend on the electronic state. Consequently the true zero-point energy must be defined in terms of the set of frequencies which are defined in terms of the *ground state* of the electronic system. It is not however this zero-point energy that really occurs in the free energy but rather the statistical average of $\sum_{\mathbf{f}} \frac{1}{2}\hbar\omega_{\mathbf{f}}$ over the electronic states that are occupied at any given temperature. This implies that $\sum_{\mathbf{f}} \frac{1}{2}\hbar\omega_{\mathbf{f}}$ will be slightly temperature dependent; it is for this reason that we speak, somewhat loosely, of a temperature dependent zero-point energy.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor R. E. Peierls for reading part of the manuscript of this article and Mr. K. Major and Mr. B. V. Thompson for considerable help with the preparation of the manuscript.

APPENDIX 1

THE MAGNITUDE OF THE NON-ADIABATIX MATRIC ELEMENTS

The matrix element $C_{nn'}$ is defined (eqn. (2.5)) as the sum of two terms $A_{nn'}$ and $B_{nn'}$. We estimate the magnitude of $A_{nn'}$. Exactly the same methods can be applied to $B_{nn'}$. Now

$$A_{nn'} = -\frac{\hbar^2}{M}\sum_j \int \psi_n^* \nabla_{\mathbf{R}_j}\psi_{n'}\, d^3\mathbf{r}\,.\,\nabla_{\mathbf{R}_j}\,. \tag{A 1.1}$$

The 'matrix element' is of course really an operator because only the electron coordinates are integrated over. What we want to do is to estimate the magnitude of the product of $A_{nn'}$ and a typical zero-order wave function $\chi_{mn'}^{(0)}$ (see eqn. (2.1)). The velocity operator of the jth ion $v_j = -(i\hbar/m)\nabla_{\mathbf{R}_j}$. So we can write

$$A_{nn'}\chi_{mn'}^{(0)} = i\hbar \sum_j \int \psi_n^* \nabla_{\mathbf{R}_j}\psi_{n'}\, d^3\mathbf{r}\,.\,\bar{v}_j\chi_{mn}^{(0)}. \tag{A 1.2}$$

When the operator $\mathbf{v}_j$ acts on $\chi_{mn'}^{(0)}$ it can be replaced by $\bar{v}$, where $\bar{v}$ is the average velocity of the ions in the lattice. A more unfavourable estimate would be to replace v_j by the maximum velocity of the ions, this would lead to only a small numerical change in our estimate. We can therefore write for the magnitude of $A_{nn'}$:

$$|A_{nn'}| \leqslant \hbar\bar{v}\,\Big|\sum_j \int \psi_n^* \nabla_{\mathbf{R}_j}\psi_{n'}\, d^3\mathbf{r}\,\Big|\,. \tag{A 1.3}$$

The Schrödinger equation for $\psi_{n'}$ is

$$H_{\mathrm{el}}\psi_{n'} = E_{n'}\psi_{n'}. \tag{A 1.4}$$

If we apply the operator $\sum_j \nabla_{\mathbf{R}_j}$ to both sides of this equation, multiply by ψ_n^* on the left and integrate over the electron coordinates, we find that

$$\sum_j \int \psi_n^* \nabla_{\mathbf{R}_j}\psi_{n'}\, d^3\mathbf{r} = \sum_j \frac{(\nabla_{\mathbf{R}_j} V_{\mathrm{int}})_{nn'}}{E_n - E_{n'}}\,, \tag{A 1.5}$$

where V_{int} is the interaction potential of the electrons with the ions. If the ions suffer displacements whose average magnitude is l, then the distortion $\delta\psi_n$ in ψ_n is given by

$$\delta\psi_n = l\sum_n \frac{\left(\sum_j \nabla_{\mathbf{R}_j} V_{\mathrm{int}}\right)_{nn'}}{E_n - E_{n'}}\,\psi_{n'}. \tag{A 1.6}$$

For an appreciable distortion we require that l satisfies

$$l\,\frac{\left(\sum_j \nabla_{\mathbf{R}_j} V_{\mathrm{int}}\right)_{nn'}}{E_n - E_{n'}} \sim 1. \tag{A 1.7}$$

Combining this relation with eqn. (A 1.5) we find that

$$\Big| \sum_j \int \psi_n{}^* \nabla_{\mathbf{R}_j} \psi_{n'} \, d^3\mathbf{r} \Big| \sim \frac{1}{l}, \qquad \text{(A 1.8)}$$

where l is the average distance the ions have to be moved to produce an appreciable distortion in ψ_n.

APPENDIX 2

THE SPIN SUSCEPTIBILITY

In a uniform magnetic field **H** we can write the lowest order correction to the free energy in the form:

$$F^{\mathrm{C}} = \sum_{\mathbf{k},\mathbf{f}} \frac{n_{\mathbf{k}}{}^+(1-n_{\mathbf{k}-\mathbf{f}}{}^+)}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}} + \sum_{k,f} \frac{n_{\mathbf{k}}{}^-(1-n_{\mathbf{k}-\mathbf{f}}{}^-)}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{f}}}; \qquad \text{(A 2.1)}$$

Here

$$n_{\mathbf{k}}{}^{\pm} = [\exp[\epsilon_{\mathbf{k}} - \eta^{\pm}/kT] + 1]^{-1}, \qquad \text{(A 2.2)}$$

where

$$\eta^{\pm} = \eta(H) \pm \mu H \qquad \text{(A 2.3)}$$

and $\eta(H)$ is the chemical potential of the system in the magnetic field. It is determined by the equation:

$$N = \sum_{\mathbf{k}} (n_{\mathbf{k}}{}^+ + \eta_{\mathbf{k}}{}^-), \qquad \text{(A 2.4)}$$

a straightforward calculation gives

$$\eta^{\pm} = \eta(0) - \frac{1}{4}\frac{\mu^2 H^2}{\eta(0)} \pm \mu H. \qquad \text{(A 2.5)}$$

This expression is accurate to second order in H. The correction $\delta\chi_{\mathrm{C}}$ to the susceptibility is given by

$$\delta\chi_{\mathrm{C}} = -\left(\frac{\partial^2 F^{\mathrm{C}}}{\partial H^2}\right)_{H=0} \qquad \text{(A 2.6)}$$

$$= -\left[\left(\frac{\partial^2 F_+{}^{\mathrm{C}}}{\partial H^2}\right)_{H=0} + \left(\frac{\partial^2 F^{\mathrm{C}}}{\partial H^2}\right)_{H=0}\right]; \qquad \text{(A 2.7)}$$

after some simple manipulations we find that

$$\delta\chi_{\mathrm{C}} = -2\mu^2 \left[\frac{\partial^2 F^{\mathrm{C}}(0)}{\partial \eta^2} + \frac{\partial^2 F_{\mathrm{T}}{}^{\mathrm{C}}(0)}{\partial \eta^2}\right]. \qquad \text{(A 2.8)}$$

In this last equation $F^{\mathrm{C}}(0)$ is the correction to the free energy at zero temperature in zero field, $F_{\mathrm{T}}{}^{\mathrm{C}}(0)$ is the correction to the free energy to order $(kT/\eta)^2$ in zero field and η is the chemical potential in zero field. Now the dependence of F^{C} on η is given by,

$$F_{\mathrm{C}} = N\eta C\left[c_s n_1 (2m/\eta)^{1/2} + n_2 \left(\frac{kT}{\eta}\right)^2\right]. \qquad \text{(A 2.9)}$$

Here n_1 and n_2 are two pure numbers of order unity, c_s is the velocity of sound and C is the electron–phonon coupling constant. The first term in the expression is of the order of $k\theta$ per particle—as we mentioned in § 4.1. The second temperature dependent term leads to the large correction to the specific heat that was also discussed in § 4.1. If we substitute this expression in (A 2.9) then we find that

$$\delta\chi_C = p_1\chi_0\left(\frac{k\theta}{\eta}\right) + p_2\chi_T C, \qquad \text{(A 2.10)}$$

where p_1 and p_2 are two numbers of order unity, χ_0 is the temperature independent Pauli susceptibility and χ_T is the temperature dependent term in the susceptibility. This is the expression on which we based our discussion in § 4.1.

APPENDIX 3

THE FUNCTION $S(\mathbf{f})$.

In this appendix we shall calculate the function

$$S(\mathbf{f}) = \sum_{\mathbf{k}} \frac{n(\mathbf{k}) - n(\mathbf{k}-\mathbf{f})}{\epsilon_{\mathbf{k}-\mathbf{f}} - \epsilon_{\mathbf{k}} + \omega_{\mathbf{f}}} \qquad \text{(A 3.1)}$$

for a free electron model. We shall show that it is negligibly different from the function

$$S^0(\mathbf{f}) = \sum_{\mathbf{k}} \frac{n(\mathbf{k}) - n(\mathbf{k}-\mathbf{f})}{\epsilon_{\mathbf{k}-\mathbf{f}} - \epsilon_{\mathbf{k}}} = 2\sum_{\mathbf{k}} \frac{n(\mathbf{k})}{\epsilon_{\mathbf{k}-\mathbf{f}} - \epsilon_{\mathbf{k}}}. \qquad \text{(A 3.2)}$$

We can write

$$S(\mathbf{f}) = \sum_{\mathbf{k}} \frac{n(\mathbf{k})}{\epsilon_{\mathbf{k}-\mathbf{f}} - \epsilon_{\mathbf{k}} + \omega_{\mathbf{f}}} + \sum_{\mathbf{k}} \frac{n(\mathbf{k})}{\epsilon_{\mathbf{k}-\mathbf{f}} - \epsilon_{\mathbf{k}} - \omega_{\mathbf{f}}}$$
$$= S_+(\mathbf{f}) + S_-(\mathbf{f}). \qquad \text{(A 3.3)}$$

Now

$$S_\pm(\mathbf{f}) = \left(\frac{2m}{\hbar^2}\right)\frac{2\pi v}{(2\pi)^3}\int_0^{\kappa_F} \kappa^2\, d\kappa \int_{-1}^{+1} \frac{dz}{2\kappa f z - f^2 \pm \alpha f}, \qquad \text{(A 3.4)}$$

where

$$\alpha = 2mc/\hbar. \qquad \text{(A 3.5)}$$

The z interaction is trivial and we find:

$$S_\pm(\mathbf{f}) = \frac{3N}{4E_F}\frac{\kappa_F}{f}\int_0^1 x\, dx \log\left|\frac{x-\lambda_\pm}{x+\lambda_\pm}\right| \qquad \text{(A 3.6)}$$

where

$$\lambda_\pm = \frac{f \mp \alpha}{2\kappa_F}. \qquad \text{(A 3.7)}$$

The remaining integration is elementary and we finally find that

$$S(\mathbf{f}) = \frac{3N}{4E_F}\frac{\kappa_F}{f}\left[\lambda_+ + \lambda_- + \tfrac{1}{2}(1-\lambda_+^2)\log\left|\frac{1+\lambda_+}{1-\lambda_+}\right| \right.$$
$$\left. + \tfrac{1}{2}(1-\lambda_-^2)\log\left|\frac{1+\lambda_-}{1-\lambda_-}\right|\right]. \qquad \text{(A 3.8)}$$

Now

$$\alpha = 2mc/\hbar \sim \frac{k\theta}{E_F}\,\kappa_R \sim 10^{-2}\kappa_F\,;$$

consequently, for all values of f, α is negligible.

We find that in the limit $|f| \to 0$,

$$S(\mathbf{f}) = \frac{3N}{2E_F}\left(1 + O(k\theta/\zeta)^2\right), \qquad \text{(A 3.9)}$$

whereas the function $S^0(\mathbf{f})$ tends to the limit:

$$\frac{3N}{2E_F}. \qquad \text{(A 3.10)}$$

The correction terms are therefore of order 10^{-4}.

Since α is negligible for all $|\mathbf{f}|$ we can set it equal to zero in our expression for $S(\mathbf{f})$. We then find that

$$S(\mathbf{f}) = \frac{3N}{2E_F}\left[\frac{1}{2} + \frac{4\kappa_F{}^2 - f^2}{8\kappa_F f}\log\left|\frac{2\kappa_R + f}{2\kappa_R - f}\right|\right]. \qquad \text{(A 3.11)}$$

The largest value of f is $2\kappa_F$ and for this value

$$S(\mathbf{f}) = 3N/4E_F. \qquad \text{(A 3.12)}$$

This is exactly one-half of its value in the limit $|f| \to 0$. It is a simple matter to show that

$$S(2\kappa_F) \leqslant S(\mathbf{f}) \leqslant S(0) \qquad \text{(A 3.13)}$$

and is a very smoothly varying function of f.

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Crystal Stability and the Theory of Ferroelectricity
Part II. Piezoelectric Crystals

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Abstract

In Part I the dielectric properties of cubic crystals with atoms in special positions were discussed, with particular reference to crystals which become unstable against a transverse optic mode of vibration of long wavelength. These considerations are now extended to crystals of general symmetry, and it is shown that the anomalous temperature dependence of certain dielectric, piezoelectric, and elastic constants in the paraelectric phase of ferroelectric crystals can be described and correlated in a very natural way in terms of crystal stability. A formula relating the dispersion frequency of the anomalous dielectric constant to the spontaneous polarization and the displacements of the atoms in a ferroelectric transition, previously derived for barium titanate, is generalized. The transitions in KH_2PO_4 and in $NH_4H_2PO_4$, and the ordering of the hydrogen atoms in these crystals, are discussed qualitatively in terms of the stability of normal modes of vibration.

§ 1. Introduction

In Part I (Cochran 1960) a ferroelectric transition in a crystal was considered in terms of the normal modes of vibration. Attention was confined to crystals which are cubic in the paraelectric phase and have atoms in special positions in the unit cell. This approach provided an interpretation of certain of the properties of crystals of the barium titanate type ; in particular it proved possible to correlate the dielectric properties with the displacements of the atoms at a transition and with the frequencies of certain normal modes of vibration of long wavelength. In Part I it was tacitly assumed that in the cubic phase each atom occupied a centre of symmetry in the crystal, which was therefore not piezoelectric. The elastic constants were not derived in terms of the parameters used to specify the short-range and the long-range (Coulomb) interactions; this could readily have been done and it would have been found that no anomalous variation with temperature was predicted. The piezoelectric and elastic constants of the ferroelectric phases were not considered. In this paper these considerations are extended to include crystals which are piezoelectric in the paraelectric phase, and which are not restricted as to structure or space group symmetry. It is however assumed in the meantime that we have to deal with a perfect crystal, that is, one which does not exhibit the kind of positional disorder found in KH_2PO_4. It is found that a lattice dynamics treatment correlates satisfactorily the properties considered in Part I, and also the anomalous temperature dependence of certain elastic constants and piezoelectric constants in the paraelectric phase. While many of the conclusions arrived at are no different from those given by the phenomenological theory of Mueller (1940) and of Cady (1946), it is of some interest to show that they can be reached by a more atomistic approach. The relations between macroscopic properties established by the thermodynamic theory and the fact that these relations are confirmed by experiment are sometimes summarized in the statement that "the piezoelectric and elastic anomalies can be considered to be consequences of the dielectric anomaly". Our object is to show that all three may be given a more fundamental interpretation in terms of crystal stability.

In § 2 we derive general equations which govern the lattice dynamics of a crystal in which the atoms are polarizable. By way of illustration, § 3 deals with the dielectric and elastic properties of the simplest type of crystal which exhibits piezoelectricity, namely the zinc-blende type. It is shown that a transition which exhibits all the characteristic features of a ferroelectric transition is in principle possible even in this type of structure. The discussion is extended to include crystals of general symmetry, in § 4. The way in which a lattice dynamics treatment must be extended to take into account special features of KH_2PO_4 and isomorphous crystals is discussed qualitatively in the final section.

§ 2. LATTICE DYNAMICS OF A CRYSTAL WITH POLARIZABLE IONS

The treatment of this problem is based on an extension of the Born–von Kármán theory made by Woods *et al.* (1960) which in turn can be related to earlier work by Mashkevich and Tolpygo (1957). It is assumed that the energy perturbation in a crystal in which the atoms are given small displacements is a quadratic function of the nuclear displacements and the electronic dipole moments. The most general expression of this form is the following:

$$\begin{aligned}\Phi_2 = -\tfrac{1}{2}\sum_{lKx}\Bigg\{\sum_{l'K'y}\big[&\Phi_{xy}{}^{(R)}(lK,l'K')u_x(lK)u_y(l'K')\\&+Y_{K'}{}^{-1}\Phi_{xy}{}^{(T)}(lK,l'K')u_x(lK)p_y(l'K')\\&+Y_K{}^{-1}\Phi_{yx}{}^{(T)}(l'K',lK)p_x(lK)u_y(l'K')\\&+Y_K{}^{-1}Y_{K'}{}^{-1}\Phi_{xy}{}^{(S)}(lK,l'K')p_x(lK)p_y(l'K')\big]\\&-\alpha_K{}^{-1}p_x{}^2(lK)+(p_x(lK)+Z_Ku_x(lK))E_x(lK)\Bigg\}. \quad . \quad (2.1)\end{aligned}$$

Here $\mathbf{u}(lK)$ denotes the displacement of the Kth atom in the lth cell, $\mathbf{p}(lK)$ its electronic dipole moment, α_K its electronic polarizability and Z_K its ionic charge (taking $+4{\cdot}8\times10^{-10}$ e.s.u. as the unit of charge), while $\mathbf{E}(lK)$ is the field due to the remainder of the crystal. In the Born theory of ionic crystals (Born and Huang 1954) the tensors $\Phi^{(T)}$ and $\Phi^{(S)}$ do not appear, and in much of the theory hitherto it has also been assumed that $\alpha_K = 0$. The additional terms involving $\Phi^{(T)}$ and $\Phi^{(S)}$ in eqn. (2.1) take account of short-range forces between *polarized* atoms. They can be interpreted within the framework of the Born–von Kármán theory in terms of a shell model in which the outer electrons are represented by a shell carrying a charge Y_K. This shell exerts short-range forces on both cores and shells of neighbouring atoms, and $\mathbf{p}(lK) = Y_K \mathbf{w}(lL)$ where $\mathbf{w}(lK)$ is the relative displacement of shell and core. It should be emphasized that this model does no more than provide a convenient nomenclature and a link with the Born–von Kármán theory; the eqns. (2.11), at which we eventually arrive, can be written so as to involve only atomic displacements and dipole moments, without mention of cores and shells. The equations of motion to be used in conjunction with eqn. (2.1) are

$$m_K \ddot{u}_x(lK) = \frac{-\partial \Phi_2}{\partial u_x(lK)}, \qquad 0 = \frac{\partial \Phi_2}{\partial p_x(lK)} \quad . \quad . \quad . \quad (2.2)$$

(Mashkevich and Tolpygo 1957). These lead to

$$\begin{aligned} m_K \ddot{u}_x(lK) = \sum_{l'K'y} &(\Phi_{xy}{}^{(R)}(lK, l'K') u_y(l'K') \\ &+ \Phi_{xy}{}^{(T)}(lK, l'K') w_y(l'K')) + Z_K E_x(lK), \\ 0 = \sum_{l'K'y} &(\Phi_{yx}{}^{(T)}(l'K', lK) u_y(l'K') + \Phi_{xy}{}^{(S)}(lK, l'K') w_y(l'K')) \\ &- \alpha_K{}^{-1} Y_K{}^2 w_x(lK) + Y_K E_x(lK). \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3) \end{aligned}$$

These may now be written in terms of travelling waves by introducing

$$\left.\begin{aligned} \mathbf{u}(lK) &= \mathbf{U}(K) \exp i(\mathbf{q}\,.\,\mathbf{r}(lK) - \omega t), \\ \mathbf{w}(lK) &= \mathbf{W}(K) \exp i(\mathbf{q}\,.\,\mathbf{r}(lK) - \omega t), \\ \mathbf{E}(lK) &= \mathscr{E}(K) \exp i(\mathbf{q}\,.\,\mathbf{r}(lK) - \omega t), \end{aligned}\right\} \quad . \quad . \quad . \quad (2.4)$$

where $q = 2\pi \div$ wavelength and $\omega = 2\pi \times$ frequency of a normal mode of vibration. The equilibrium position of an atom is

$$\mathbf{r}(lK) = \mathbf{r}(l) + \mathbf{r}(K), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.5)$$

where $\mathbf{r}(l)$ is a lattice translation.

We also define the 'coefficients' of the short-range interaction by

$$R_{xy}(KK') = -\sum_{l'} \Phi_{xy}{}^{(R)}(lK, l'K') \exp i\mathbf{q}\,.\,(\mathbf{r}(l'K') - \mathbf{r}(lK))$$

and similarly for

$$T_{xy}(KK') \quad \text{and} \quad S_{xy}(KK'), \quad . \quad . \quad . \quad (2.6)$$

while the corresponding coefficients of the Coulomb interaction are defined by

$$C_{xy}(KK') = -\exp i\mathbf{q}\,.\,(\mathbf{r}(K') - \mathbf{r}(K)) \lim_{\mathbf{r} \to \mathbf{r}(K) - \mathbf{r}(K')} \times \left\{ \sum_l \frac{\partial^2}{\partial x\, \partial y} \left(\frac{1}{|\mathbf{r} - \mathbf{r}(l)|} \right) \exp i\mathbf{q}\,.\,\mathbf{r}(l) \right\} \quad . \quad . \quad . \quad (2.7)$$

(Kellermann 1940).

The amplitude of the electric field is then found to be given by

$$\mathscr{E}_x(K) = -\sum_{K'y} C_{xy}(KK')(Z_{K'}U_y(K') + Y_{K'}W_y(K')). \qquad (2.8)$$

and the equations of motion reduce to

$$\begin{aligned} \omega^2 m_K U_x(K) = {} & \sum_{K'y} (R_{xy}(KK') + Z_K Z_{K'} C_{xy}(KK'))U_y(K') \\ & + \sum_{K'y} (T_{xy}(KK') + Z_K Y_{K'} C_{xy}(KK'))W_y(K'), \\ 0 = {} & \sum_{K'y} (T^*_{yx}(K'K) + Y_K Z_{K'} C_{xy}(KK'))U_y(K') \\ & + \sum_{K'y} (\mathscr{S}_{yx}(KK') + Y_K Y_{K'} C_{xy}(KK'))W_y(K'), \end{aligned} \qquad (2.9)$$

where

$$\mathscr{S}_{xy}(KK') = S_{xy}(KK') + \delta_{xy}\delta_{KK'}\alpha_K^{-1} Y_K^2. \quad . \quad . \quad (2.10)$$

The eqns. (2.9) apply as they stand for crystals which are diagonally cubic. For crystals of lower symmetry the coefficients $C_{xy}(KK')$, (eqn. (2.7)), and $\mathscr{S}_{xy}(KK')$ (eqns. (2.6) and (2.10)) must be re-defined for $K = K'$. The details are however not important for our present purpose and will be given elsewhere.

Equations (2.9) can be written in matrix notation as

$$\left.\begin{aligned} \omega^2 \mathbf{m}_\mathrm{d}\mathbf{U}_\mathrm{c} &= (\mathbf{R} + \mathbf{Z}_\mathrm{d}\mathbf{C}\mathbf{Z}_\mathrm{d})\mathbf{U}_\mathrm{c} + (\mathbf{T} + \mathbf{Z}_\mathrm{d}\mathbf{C}\mathbf{Y}_\mathrm{d})\mathbf{W}_\mathrm{c}, \\ 0 &= (\tilde{\mathbf{T}}^* + \mathbf{Y}_\mathrm{d}\mathbf{C}\mathbf{Z}_\mathrm{d})\mathbf{U}_\mathrm{c} + (\mathscr{S} + \mathbf{Y}_\mathrm{d}\mathbf{C}\mathbf{Y}_\mathrm{d})\mathbf{W}_\mathrm{c}, \end{aligned}\right\} \qquad (2.11)$$

where $\tilde{\mathbf{T}}$ is the transposed matrix obtained by interchanging rows and columns of $\mathbf{T}$. As in Part I, subscript d denotes a diagonal and c a column matrix. Other matrices such as $\mathbf{R}$ are square matrices of order $3n \times 3n$, where n is the number of atoms per unit cell. These equations are nearly identical in form with those given in Part I (p. 406), they are, however, much more general in that they now apply to a crystal of any symmetry and for any value of the wave vector $\mathbf{q}$. The corresponding equations of Part I involved matrices of order $n \times n$, they applied only for $\mathbf{q} \to 0$ and to purely transverse modes of vibration. A simplifying assumption made in Part I also resulted in $\tilde{\mathbf{T}} = \mathbf{T}$, in the present notation.

It has now been shown by Cowley (1961 a) that eqns. (2.11), which have been derived here from the potential function (2.1), can also be derived by a purely wave-mechanical treatment of the motions of the electrons and nuclei, provided that quadrupole and higher moments of the electron distribution are neglected.

§ 3. DIELECTRIC AND ELASTIC PROPERTIES OF THE ZINC BLENDE STRUCTURE

In Part I it was found useful to discuss the lattice dynamics of a diatomic crystal of the sodium chloride or of the caesium chloride type. It was shown that with a suitable choice of the parameters governing the lattice dynamics of such a crystal, it would exhibit dielectric and other properties closely paralleling those of barium titanate. In this section we show that the same choice of parameters for a crystal of the zinc-blende type will cause it to exhibit properties typical of the paraelectric phase of a piezoelectric crystal approaching a ferroelectric transition. A crystal of this class has three elastic constants C_{11}, C_{12} and C_{44}. It can be shown from the theory of elasticity, and also by the methods used here, that $C_{11}{}^{\mathrm{E}} = C_{11}{}^{\mathrm{D}}$, $C_{12}{}^{\mathrm{E}} = C_{12}{}^{\mathrm{D}}$ but $C_{44}{}^{\mathrm{E}} \neq C_{44}{}^{\mathrm{D}}$. There is only one piezoelectric constant e_{14}. The clamped and free dielectric constants ϵ_{S}'' and ϵ_{S}' differ, there is however only one dielectric constant ϵ_{e} at optical frequencies. The two atoms per (primitive) unit cell will be identified by $K=1$ at the origin, $K=2$ at $(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})r_0$ where $2r_0$ is the (cubic) unit cell dimension. When the wave-vector $\mathbf{q}$ is in a direction such as [100] the 6×6 matrices of eqn. (2.11) can each be separated into three 2×2 matrices which separately describe the longitudinal and two transverse modes, for each of which the form of the equations of motion is still as given by eqn. (2.11).

The macroscopic properties of the crystal can be derived quite simply, from these 'one-dimensional' equations. The dielectric properties follow from equations already given in Part I. The static polarizability is given by $\alpha_{\mathrm{S}} = \alpha_{\mathrm{i}} + \alpha_{\mathrm{e}}$, where α_{e} is the electronic polarizability (of one unit cell) and the ionic polarizability is given by

$$\alpha_{\mathrm{i}} = (Z_1')^2/R_0'. \qquad \qquad (3.1)$$

In this equation the effective charge Z_1', and the effective short-range force constant R_0' between Bravais arrays of atoms, are as defined in Part I. The (clamped) dielectric constant is then given by the Clausius–Mossotti relation

$$\epsilon_{\mathrm{S}}'' = \frac{1+8\pi\alpha_{\mathrm{S}}/(3v)}{1-4\pi\alpha_{\mathrm{S}}/(3v)}, \qquad \qquad (3.2)$$

where $v = 2r_0{}^3$ is the volume of the unit cell. A similar relation gives the high-frequency dielectric constant ϵ_{e} in terms of α_{e}, which is in turn related to atomic parameters as in Part I. The (circular) frequencies ω_{L} and ω_{T} of longitudinal and transverse optic modes for which the wave-vector $\mathbf{q}$ tends to zero are given by

$$\left.\begin{aligned} \mu\omega_{\mathrm{L}}{}^2 &= R_0' + 8\pi(\epsilon_{\mathrm{e}}+2)(Z_1')^2/(9v\epsilon_{\mathrm{e}}), \\ \mu\omega_{\mathrm{T}}{}^2 &= R_0' - 4\pi(\epsilon_{\mathrm{e}}+2)(Z_1')^2/(9v), \end{aligned}\right\} \qquad (3.3)$$

again as in Part I.

The elastic constants can be derived by considering the limiting value of the ratio ω/q for acoustic modes propagating in different symmetry directions in the crystal. To obtain explicit expressions for the elastic constants some assumption must be made about the short-range force constants between the atoms. We shall make the simplest one, namely that there are non-Coulomb forces only between nearest-neighbour atoms in the crystal. There are then only two independent force constants,

$\Phi_{xx}^{(R)}(12)$, $\Phi_{xy}^{(R)}(12)$ and of course corresponding quantities with superscripts (T) and (S) (eqn. (2.1)). Comparatively simple expressions for C_{44} and for e_{14} are not obtained unless it is assumed that

$$\Phi_{xy}^{(R)}(12)/\Phi_{xx}^{(R)}(12)=\Phi_{xy}^{(T)}(12)/\Phi_{xx}^{(T)}(12). \quad . \quad . \quad (3.4)$$

It was found necessary to make this assumption in order to account for the measured elastic constants of germanium (Cochran 1959), it is therefore a reasonable one in the present context and is included in what follows in this section. The elastic constants may be more conveniently expressed in terms of the ratio (3.4), for which we shall write γ, and a parameter

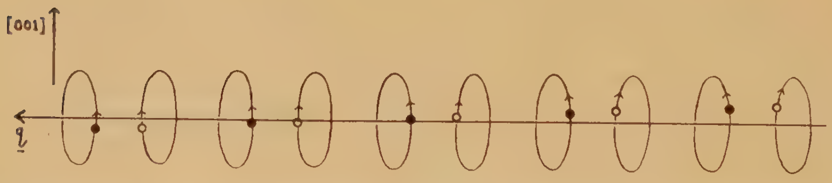
$$R_0=4\Phi_{xx}^{(R)}(12) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.5)$$

(R_0 is also an element of the matrix $\mathbf{R}$ for $\mathbf{q}=0$). The elastic constants involved, for acoustic waves travelling in different directions, are shown in the following table.

Direction of $\mathbf{q}$	Direction of (predominant) motion of atoms	Direction of electric polarization	Elastic constant
100	100	—	C_{11}
110	$1\bar{1}0$	—	$\frac{1}{2}(C_{11}-C_{12})$
100	001	010	C_{44}^{E}
110	001	110	C_{44}^{D}

The explanation in lattice dynamics terms of the different electrical conditions which result in the appearance of C_{44}^{E} in one instance and of C_{44}^{D} in the other is as follows. Although the corresponding modes are described in elasticity theory as transverse, the polarization, in the sense of the motion of the atoms, is in fact elliptic with the ratio of minor to major axis proportional to wave-number q. The axes of the ellipse are oriented as shown in fig. 1. Atoms $K=1$ and $K=2$ describe ellipses in

Fig. 1



Displacement and direction of motion of successive planes of atoms near a node of an acoustic wave in the zinc blende structure. When $\mathbf{q}$ is parallel to [100] the minor axis of each ellipse is parallel to [010] but when $\mathbf{q}$ is parallel to [110] the minor axis is also parallel to [110]. The two types of dot denote the two types of atom.

opposite senses and since they are oppositely charged a wave of electrical polarization results which in one instance (third line of the table) is transverse but in the other (fourth line of the table) is longitudinal. The former gives no macroscopic electric field, the latter produces a macroscopic field of amplitude $-4\pi\mathscr{P}$, where $\mathscr{P}$ is the amplitude of the polarization wave. A detailed derivation of the elastic constants will not be given here, the method is similar in principle to that used to derive the elastic constants of germanium (Cochran 1959). The correctness of the results has subsequently been checked against the more general results obtained by Cowley (1961 b). The elastic constants C_{11} and C_{12} are found to be independent of the electronic polarizability and are given by

$$C_{11}=\frac{1}{r_0}(R_0/8+0{\cdot}13\,Z_1^2/v), \qquad (3.6)$$

$$C_{12}=\frac{1}{r_0}(R_0(2\gamma-1)/8-1{\cdot}32\,Z_1^2/v). \qquad (3.7)$$

The expressions for $C_{44}{}^{\mathrm{E}}$ and $C_{44}{}^{\mathrm{D}}$ are considerably simplified by writing them so as to involve ϵ_{S}'', thus:

$$C_{44}{}^{\mathrm{E}}=\frac{1}{r_0}(R_0(1-\gamma^2)/8+2{\cdot}96Z_1^2/v-2\pi(\epsilon_{\mathrm{S}}''+2)(1{\cdot}20-\tfrac{1}{2}\gamma)^2Z_1^2/(9v)), \qquad (3.8)$$

$$C_{44}{}^{\mathrm{D}}=\frac{1}{r_0}(R_0(1-\gamma^2)/8-1{\cdot}57Z_1^2/v+4\pi(\epsilon_{\mathrm{S}}''+2)(0{\cdot}60+\tfrac{1}{2}\gamma)^2Z_1^2/(9v\epsilon_{\mathrm{S}}'')). \qquad (3.9)$$

The piezoelectric constant e_{14} can be derived in a similar way by considering an acoustic wave propagating in the [100] direction, with the atomic displacements along [011]. In this case the electric polarization is also along [011] and arises from the fact that the atoms $K=1$ and $K=2$ do not move in phase. The ratio of polarization to strain gives the piezoelectric constant e_{14} since the macroscopic field is zero. The result obtained is

$$e_{14}=(Z_1r_0(\epsilon_{\mathrm{S}}''+2)/(3v))(5{\cdot}03\alpha_{\mathrm{S}}/v-\tfrac{1}{2}\gamma), \qquad (3.10)$$

where α_{S} and ϵ_{S}'' are related by eqn. (3.2).

We now have rather more than the necessary number of relations between atomic parameters and macroscopic constants. The latter should be related by the following results

$$\omega_{\mathrm{L}}{}^2/\omega_{\mathrm{T}}{}^2=\epsilon_{\mathrm{S}}''/\epsilon_{\mathrm{e}} \qquad (3.11)$$

(Lyddane *et al.* 1941) and

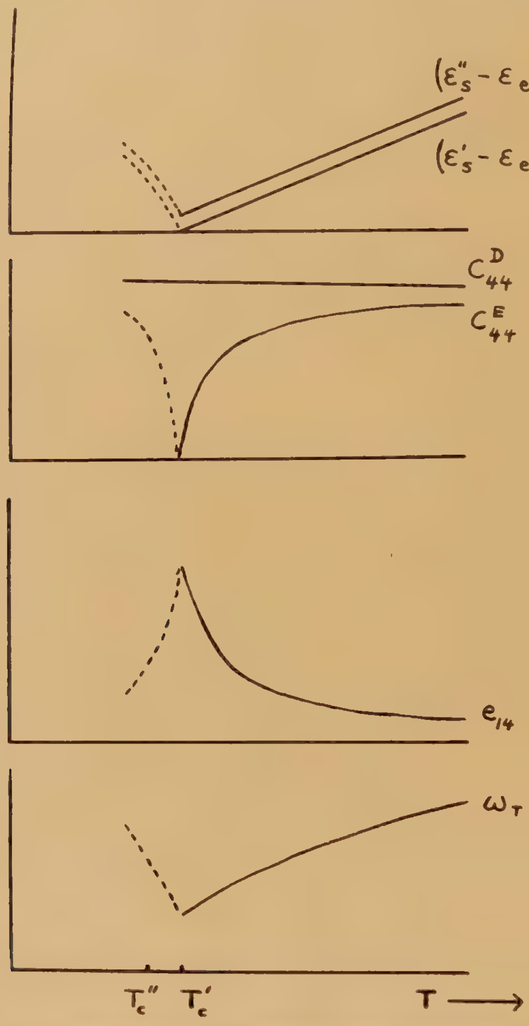
$$C_{44}{}^{\mathrm{D}}-C_{44}{}^{\mathrm{E}}=4\pi e_{14}{}^2/\epsilon_{\mathrm{S}}'' \qquad (3.12)$$

(Cady 1946). The first of these is known to be satisfied for this model of a crystal (Woods *et al.* 1960), and the second is also found to hold, which provides a useful check on the derivation of eqns. (3.8), (3.9) and (3.10). Other macroscopic constants could be calculated directly in terms of atomic parameters, but as in the above two instances, they cannot differ from those given by the relations of the phenomenological theory. It is therefore simpler to obtain ϵ_S', the free dielectric constant, from the relation

$$\epsilon_S' = \epsilon_S'' C_{44}^{\mathrm{D}}/C_{44}^{\mathrm{E}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.13)$$

(Cady 1946), since all quantities on the right-hand side of (3.13) have already been calculated.

Fig. 2



The variation with temperature of certain quantities when the frequency ω_{T} varies as shown in the lowest graph, for the zinc blende structure.

Now let us suppose, exactly as in § 2 of Part I, that the force constants happen to be such that ω_{T} (eqn. (3.3)) is close to zero, but other frequencies are comparatively high, and furthermore that the force constants and/or unit cell volume, etc., vary linearly with temperature so that

$$1-4\pi(\epsilon_{\mathrm{e}}+2)(Z_1')^2/(9vR_0')\equiv\mu\omega_{\mathrm{T}}^2/R_0'=\beta(T-T_{\mathrm{c}}''), \qquad (3.14)$$

where β is a temperature coefficient of the same order of magnitude as the volume coefficient of expansion. The temperature T_{c}'' is then that at which the crystal would become unstable against a transverse optic mode for which the wave-number is near zero. As in Part I, ϵ_{S}'' will then follow a Curie–Weiss law with the Curie constant

$$\mathscr{C}=(\epsilon_{\mathrm{e}}+2)/(4\pi\beta). \quad . \quad . \quad . \quad . \quad . \quad (3.15)$$

It also follows from the expressions derived above for the various other macroscopic quantities that their temperature variations will be as shown qualitatively by the full lines in fig. 2. In terms of crystal stability, what happens is as follows. Before the crystal can become unstable against a transverse optic mode, it becomes unstable against a transverse *acoustic* mode, since the expression for C_{44}^{E} contains a term which depends on ϵ_{S}''. This term causes C_{44}^{E} to vanish at a temperature T_{c}', greater than T_{c}'', and given approximately by

$$T'_{\mathrm{c}}\simeq T_{\mathrm{c}}''+\frac{8\pi^2\mathscr{C}Z_1^2(1\cdot20-\frac{1}{2}\gamma)^2}{9vr_0C_{44}^{\mathrm{D}}}. \quad . \quad . \quad . \quad . \quad (3.16)$$

The free dielectric constant therefore becomes infinite at this temperature (eqn. (3.13)) and the crystal shears spontaneously about a crystallographic axis, while positive and negative ions move in opposite directions along this axis (see the third line of the table). The distinction between C^{D} and C^{E} can only be made for waves whose wavelength is small compared with the length of the crystal itself; the effective elastic constant for longer waves depends on the electrical boundary conditions. It follows that the crystal must become unstable against a mode whose wavelength is smaller than the crystal, which will therefore develop domains of alternate direction of shear and of polarization. These conclusions, and the features of fig. 2 shown by the full lines, follow from the theory of lattice dynamics, and one assumption, eqn. (3.14).

One further assumption is necessary if the crystal is not to become completely unstable, and the same assumption determines the properties of the polarized phase. It is that the short-range force per atom between Bravais arrays displaced a comparatively large distance u is anharmonic,

$$F(u)=R_0'u+Bu^3+B'u^5+\ldots. \quad . \quad . \quad . \quad (3.17)$$

The relation between applied field E_{A} and polarization P (for the cubically clamped crystal) can then be shown to be

$$E_{\mathrm{A}}=P(T-T_{\mathrm{c}}'')/\mathscr{C}+v^3BP^3/(Z_1'')^4+v^5B'P^5/(Z_1'')^6+\ldots, \qquad (3.18)$$

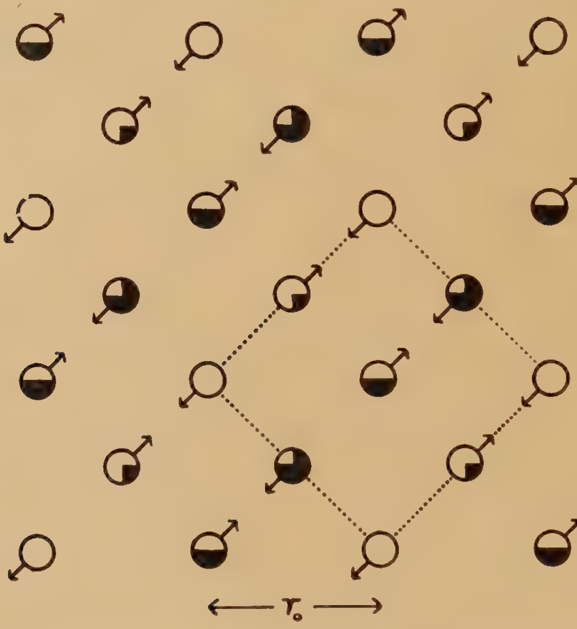
where the apparent charge Z_1'' is defined by

$$Z_1''=Z_1'(\epsilon_e+2)/3 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (3.19)$$

(see Part I). The assumption (3.17) enables the curves of fig. 2 to be continued as shown qualitatively by the dotted lines.

A crystal having the zinc-blende structure may in principle become unstable against other modes of vibration than the particular transverse optic mode considered above. Suppose an instability occurs, as a result of a linear variation of force constants with temperature, for a transverse mode for which $\mathbf{q}$ is at the boundary of the first Brillouin zone in the [001] direction, that is, $\mathbf{q}=(0, 0, \pi/r_0)$. In this mode the atoms move as shown in fig. 3 and such an instability would result in an antiferroelectric transition.

Fig. 3



Direction of displacement of the atoms in the zinc blende structure in a transverse mode for which $\mathbf{q}=(0, 0, \pi/r_0)$. The unit cell dimension perpendicular to the plane of the diagram is $2r_0$, and atoms at heights 0, $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$ are shown by different amounts of shading. Atoms of type 1 are at heights 0 and $\frac{1}{2}$, of type 2 at heights $\frac{1}{4}$ and $\frac{3}{4}$.

Calling the frequency of this mode ω_A, the transition will take place at a temperature T_A for which $\omega_A \simeq 0$. If $T_A \gg T_c''$, in other words if the force constants are such that $\omega_T \gg \omega_A$, the crystal will exhibit no large anomaly in ϵ_s'' or in $C_{44}{}^E$. If however ω_T and ω_A are simultaneously low, but the latter is the lower, then the variation of ϵ_s'' and of $C_{44}{}^E$ will not be very different from that shown in fig. 2, except that $C_{44}{}^{E}$ will not become zero unless $T_A < T_c'$. This particular mode has been discussed because it appears to be closely analogous to that against which $NH_4H_2PO_4$ becomes unstable. As shown in fig. 3, the zinc-blende structure can be referred to a tetragonal unit cell with $a = \sqrt{2}r_0$, $c = 2r_0$ and containing two each of atoms of type 1 and type 2. This unit cell is preserved after the transition, but is not then body-centred.

In the following section we consider how some of these results may be extended to crystals of general symmetry.

§ 4. General Theory of Dielectric and Elastic Properties

The theory of the dielectric and elastic properties of crystals has been worked out by Born and Huang (1954) in terms of lattice dynamics for the rigid ion model. Their theory has been extended by Cowley (1961 b) to include the effects of polarizability; the results are then rather complicated and their significance for ferroelectric crystals can be more readily appreciated by discussing the rigid ion model, where the same principles apply but the equations simplify considerably. For the rigid ion model eqn. (2.11) becomes simply

$$\omega^2 \mathbf{m}_d \mathbf{U}_c = (\mathbf{R} + \mathbf{Z}_d \mathbf{C} \mathbf{Z}_d) \mathbf{U}_c. \qquad . \quad . \quad . \quad . \quad (4.1)$$

It follows from the work of Born and Huang that for the discussion of modes of small wave-number it is important to separate the matrix $\mathbf{R} + \mathbf{Z}_d \mathbf{C} \mathbf{Z}_d$ into a part which is regular in $\mathbf{q}$ and a part which is not. Equation (4.1) may then be written

$$\omega^2 \mathbf{m}_d \mathbf{U}_c = \mathbf{M} \mathbf{U}_c - \mathbf{Z}_d \mathbf{E}_c, \qquad . \quad . \quad . \quad . \quad (4.2)$$

where $\mathbf{E}_c$ is a column matrix whose elements give the amplitude of the macroscopic electric field at each atomic site. (By restricting attention to transverse modes in Part I this term was excluded.) The matrix $\mathbf{M}$ may be expanded in powers of $\mathbf{q}$:

$$\mathbf{M} = \mathbf{M}^{(0)} + i \sum_{\gamma} \mathbf{M}_{\gamma}{}^{(1)} q_{\gamma} + \tfrac{1}{2} \sum_{\gamma\lambda} \mathbf{M}_{\gamma\lambda}{}^{(2)} q_{\gamma} q_{\lambda}. \qquad . \quad . \quad (4.3)$$

(In order to facilitate comparison with the results of Born and Huang, $\alpha\beta\gamma$ will be used to denote direction instead of *xyz* of earlier sections and Part I.)

The matrix $\mathbf{M}^{(0)}$ is of order $3n \times 3n$ and is singular. An effective inverse of $\mathbf{M}^{(0)}$ may be defined by constructing a matrix $\mathbf{H}^{(0)}$ whose elements satisfy the relations

$$H_{\alpha\beta}{}^{(0)}(KK') = 0 \quad \text{for} \quad K = 1 \quad \text{or} \quad K' = 1,$$
$$\sum_{K'\beta} H_{\alpha\beta}{}^{(0)}(KK') M_{\beta\gamma}{}^{(0)}(K'K'') = \delta_{\alpha\gamma} \delta_{KK''} \quad \text{for} \quad K, K', K'' = 2, 3 \ldots n. \qquad (4.4)$$

The following results may now be obtained by specializing Cowley's (1961 b) results to the rigid ion model, or by expressing those of Born and Huang (1954) in matrix notation.

The elastic constants are given by

$$C_{\alpha\gamma\beta\lambda}{}^{\mathrm{E}}=[\alpha\beta,\gamma\lambda]+[\beta\gamma,\alpha\lambda]-[\beta\lambda,\alpha\gamma]+(\alpha\gamma,\beta\lambda)$$

where

$$[\alpha\beta,\gamma\lambda]=\frac{1}{2v}\sum_{KK'}(\mathbf{M}_{\alpha\beta}{}^{(2)})_{\gamma\lambda}$$

and

$$(\alpha\gamma,\beta\lambda)=-\frac{1}{v}\sum_{KK'}(\tilde{\mathbf{M}}_{\gamma}{}^{(1)}\mathbf{H}^{(0)}\mathbf{M}_{\lambda}{}^{(1)})_{\alpha\beta}, \quad . \quad . \quad . \quad (4.5)$$

the piezoelectric constants are given by

$$e_{\beta,\alpha\gamma}=-\frac{1}{v}\sum_{KK'}(\tilde{\mathbf{M}}_{\gamma}{}^{(1)}\mathbf{H}^{(0)}\mathbf{Z}_{\mathrm{d}})_{\alpha\beta} \quad . \quad . \quad . \quad . \quad (4.6)$$

and the elements of the (clamped) static susceptibility tensor by

$$\chi_{\alpha\beta}=\frac{1}{v}\sum_{KK'}(\mathbf{Z}_{\mathrm{d}}\mathbf{H}^{(0)}\mathbf{Z}_{\mathrm{d}})_{\alpha\beta}. \quad . \quad . \quad . \quad . \quad . \quad (4.7)$$

Each of the above summations is over all matrix elements with certain subscripts held constant, e.g.

$$\sum_{KK'}(\mathbf{X})_{\alpha\beta} \quad \text{denotes} \quad \sum_{KK'}X_{\alpha\beta}(KK').$$

Next consider the solutions ω_j of the equations

$$\omega^2\mathbf{m}_{\mathrm{d}}\mathbf{U}_{\mathrm{c}}=\mathbf{M}^{(0)}\mathbf{U}_{\mathrm{c}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.8)$$

Three of these frequencies ($j=1$, 2, 3) are zero. The remaining ($3n-3$) frequencies are the dielectric dispersion frequencies. These frequencies are also the frequencies of modes of vibration for which the wavevector is perpendicular to an axis of the crystal and for which the electrical polarization is transverse, so that the macroscopic field is zero. They are therefore the infra-red absorption frequencies for special directions of the wavevector (Cochran and Cowley, to be published). Finally it may be shown that if $\mathscr{P}(j)$ is the amplitude of the polarization wave associated with the mode whose frequency is ω_j, and $\mathbf{U}(Kj)$ the corresponding amplitude of displacement of the Kth atom, the susceptibility at any frequency ω can be written

$$\chi_{\alpha\beta}(\omega)=v\sum_{j}\frac{\mathscr{P}_{\alpha}(j)\mathscr{P}_{\beta}(j)}{\sigma_j(\omega_j{}^2-\omega^2)} \quad . \quad . \quad . \quad . \quad . \quad (4.9)$$

where

$$\sigma_j=\sum_{K\gamma}m_K|U_{\gamma}(Kj)|^2. \quad . \quad . \quad . \quad . \quad (4.10)$$

The absolute magnitudes of the $U_{\gamma}(Kj)$ are of course arbitrary; it is convenient to introduce normalized values $\hat{U}_{\gamma}(Kj)$ such that

$$\sum_{K\gamma}m_K|\hat{U}_{\gamma}(Kj)|^2=1. \quad . \quad . \quad . \quad . \quad . \quad (4.11)$$

To appreciate the significance of these known results, for ferroelectric crystals one further result is required. It may be shown (see, for example, Born 1942) that if $e_\alpha(Kj)$ are the eigenvectors and ω_j^2 the eigenvalues of a matrix **D** appearing in the equations

$$\omega^2 e_\alpha(K) = \sum_{K'\beta} D_{\alpha\beta}(KK')e_\beta(K'), \qquad (4.12)$$

then

$$\sum_j \omega_j^{2p} e_\alpha(Kj)e_\beta(K'j) = (\mathbf{D}^p)_{\alpha\beta}(KK'), \qquad (4.13)$$

where the right-hand side of eqn. (4.13) is an element of the matrix (**D** raised to the power p). Applying this result to eqn. (4.8) with $p = -1$, and remembering that $\mathbf{H}^{(0)}$ is the effective inverse of $\mathbf{M}^{(0)}$, one finds that

$$\sum_{j=4}^{3n} \omega_j^{-2} \hat{U}_\alpha(Kj)\hat{U}_\beta(K'j) = H_{\alpha\beta}^{(0)}(KK'). \qquad (4.14)$$

This result enables the elements of the matrix $\mathbf{H}^{(0)}$ to be expressed in terms of the dielectric dispersion frequencies. Suppose we now have to deal with a crystal which is nearly unstable against an optic mode of vibration for which $q \to 0$, and for which the electrical polarization is transverse. We shall refer to this as the ferroelectric mode and denote it by $j = F$. Furthermore let us assume that the frequency ω_F varies with temperature according to the law

$$\omega_F^2 \propto (T - T_c''), \qquad (4.15)$$

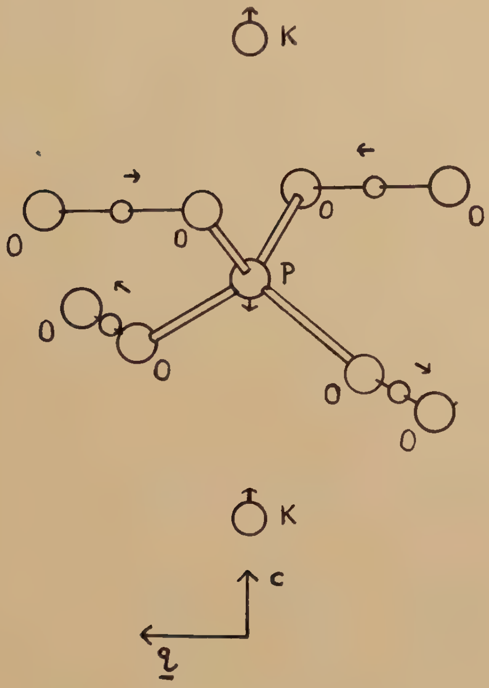
which, by analogy with the simple structures already considered, is to be expected if the force constants and unit cell volume vary linearly with temperature. If these quantities have a comparatively small temperature coefficient ($\sim 10^{-4}$ per °K, say) there will be no rapid variation of individual elements of the matrix $\mathbf{M}^{(0)}$, and the values of the $\hat{U}_\alpha(Kj)$ will remain nearly constant, even for $j = F$. From eqn. (4.14) however we see that the term ω_F^{-2} will cause certain elements of the matrix $\mathbf{H}^{(0)}$ to vary rapidly with temperature, in fact to follow a Curie–Weiss law when eqn. (4.15) is satisfied. Since the matrix $\mathbf{H}^{(0)}$ appears in eqns. (4.5), (4.6) and (4.7) it follows that certain elements of the $(\alpha\gamma, \beta\lambda)$, $e_{\beta,\alpha\gamma}$ and $\chi_{\alpha\beta}$ tensors will follow a Curie–Weiss law. This will not be the case for all elements of these tensors, for the symmetry of the crystal makes the contribution of ω_F to certain elements identically zero. As an example, consider a crystal having the symmetry of KH_2PO_4 (in the paraelectric phase). If the ferroelectric mode has $\mathscr{P}_\alpha(F) = \mathscr{P}_\beta(F) = 0$, $\mathscr{P}_\gamma(F) \neq 0$, so that **q** is perpendicular to the c-axis, then the macroscopic quantities which exhibit an anomalous temperature dependence are $(\alpha\beta, \alpha\beta) = C_{66}^E - C_{66}^P$, $e_{\gamma\alpha\beta} = e_{36}$ and $\chi_{\gamma\gamma} = \chi_3$ in the usual notation. The crystal will not make a ferroelectric transition at $T = T_c''$ however, nor will the frequency ω_F ever become precisely zero. This is because the 'internal strain' term $(\alpha\beta, \alpha\beta)$ contributes negatively to C_{66}^E (eqn. (4.5)) and causes the latter to vanish at a temperature $T_c' > T_c''$. The wavelength of the acoustic mode against which the crystal becomes unstable must be small compared with the length of the crystal in the direction of **q**, so that the pattern of spontaneous polarization and shear will be that which is found experimentally for KH_2PO_4 (Känzig 1957). If the crystal could be 'tetragonally clamped' the transition would take place at $T = T_c''$ by the crystal becoming unstable against the ferroelectric mode.

These conclusions have been reached by considering the rigid ion model of a crystal, which is not physically realistic. When electronic polarizability is taken into account, to give eqns. (2.11), the conclusions are unchanged. In eqn. (4.2) the matrix **M** must be redefined in a way analogous to the definition of **M′** in Part I, and $\mathbf{Z}_d$ replaced by a matrix which is not diagonal. Additional terms then appear on the right-hand sides of eqns. (4.5) to (4.7) (Cowley 1961 b). These additional terms are not however related to dispersion frequencies of the lattice, although they can in principle be related to electronic dispersion frequencies. They would not therefore be expected to show more than a weak temperature dependence. Equation (4.9) remains unchanged in form, but now gives the ionic susceptibility, that is, the difference between the total and high frequency (or electronic) susceptibilities.

§ 5. Discussion

The first point requiring discussion is the extent to which the foregoing constitutes a general 'theory' of ferroelectricity. The concept of crystal stability enables the salient features of a ferroelectric (or an antiferroelectric) transition to be described and correlated in a very natural way. It leaves open the explanation of the temperature variation of the frequency ω_F, except to show that this can be brought about in a variety of ways such as the temperature dependence of the volume of the unit cell or high frequency dielectric constant, or a change in the effective values of the parameters specifying the short-range interaction, either because of the anharmonicity of the lattice vibrations or because of a change of bond character with temperature, as suggested by Megaw (1952). The theory is based essentially on the harmonic approximation, in which for every mode of vibration the atoms make small oscillations about one equilibrium position in the paraelectric phase. As such it is probably adequate for ferroelectrics of the perovskite type for example. It fails to account for certain features of the transitions in other crystals, and the direction in which it must be specialized in particular cases can be illustrated by discussing qualitatively the special features of KH_2PO_4. The description of the transition which the pseudo-harmonic approximation gives for this crystal is that in the ferroelectric mode the atoms move as shown in fig. 4 with the centre of the hydrogen bond as the equilibrium position of the proton. The pattern of first-order displacements in the acoustic mode controlled by the elastic constant C_{66}^E is the same (see below). Approximately this pattern of displacement is 'frozen in' below the temperature T_c' at which the acoustic mode becomes unstable. The hydrogen atoms are not ordered from a disordered configuration. This simple picture conflicts with the spectroscopic evidence that the length of the OH bond remains nearly constant. Blinc (1960) has summarized, and used as a basis of a theory of ferroelectricity in certain crystals, the evidence that the proton in a short hydrogen bond 'tunnels' in a potential field which has a double minimum. The potential 'hump' however is not

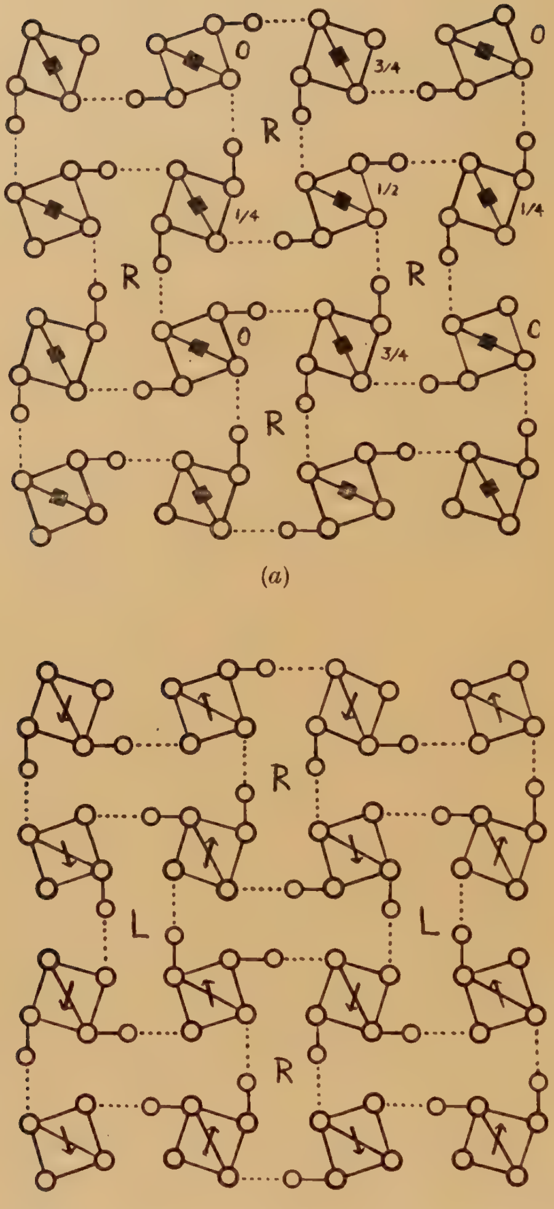
Fig. 4



Displacement of the atoms in the ferroelectric mode of vibration of KH_2PO_4, i.e. values of $\mathbf{U}(K, j=F)$, deduced from the structure analysis of Bacon and Pease. The hydrogen atoms are shown in the centres of the hydrogen bonds, but it is suggested that $\mathbf{U}(K=H, j=F)$ is nearly independent of the actual positions of hydrogen atoms within the bonds, as shown in fig. 6.

something which is independent of the position and state of polarization of the other atoms. Reid (1959) has emphasized that if, as appears very probable, configurations with other than two hydrogens immediately adjacent to a phosphate group are energetically very unfavourable, then there is no double minimum for the motion of a single proton, but only for the collective movement of a group. In the polarized phase the arrangement of the hydrogen atoms is as shown in fig. 5 (*a*) (Bacon and Pease 1955); in the antiferroelectric structure of $NH_4H_2PO_4$, according to Nagamiya (1952), it is as shown in fig. 5 (*b*). These are characterized by

Fig. 5



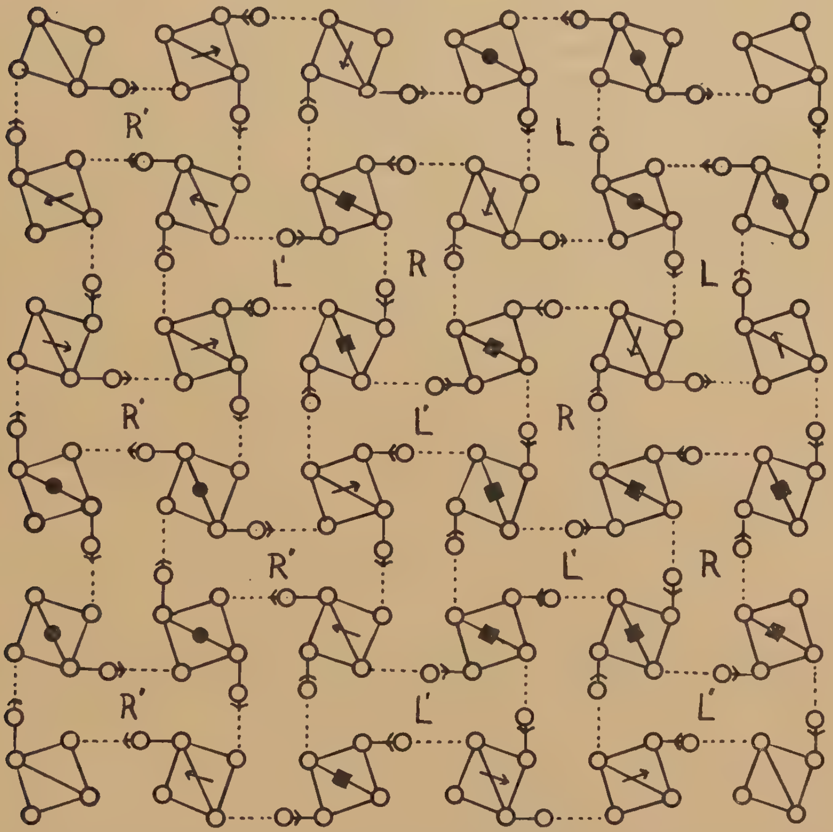
(*a*)

(*b*)

(*a*) Positions of the hydrogen atoms in the ferroelectric structure, showing spirals of hydrogen bonds all of one kind. The heights of the centres of the PO_4 tetrahedra are shown. (*b*) In the antiferroelectric structure R and L type spirals of hydrogen bonds occur alternately. Arrows indicate the dipole moments of H_2PO_4 groups.

the arrangement of hydrogen atoms in the spirals of hydrogen bonds denoted by the letters R and L. Interconversion of R and L would reverse the polarization in both cases. We suggest that in the tetragonal phase the spirals R and L, and similar arrangements producing horizontally directed dipoles, occur at random as illustrated in fig. 6. The dipole moments shown will be much smaller in this phase because of the absence of any cooperative effect. It appears plausible that the displacements of the hydrogen atoms in the ferroelectric mode are *small* displacements about their various equilibrium positions, as shown in fig. 6, while the other atoms move as in fig. 4. The ferroelectric mode then appears, in Reid's terminology, as a collective movement for which the potential hump is greatly reduced, so that in addition to their small movements, groups of

Fig. 6



Segment of a possible structure of the paraelectric phase. A small square in the centre of a PO_4 tetrahedron indicates a dipole moment down into the plane of the diagram, a small circle indicates an upward dipole moment. Arrows attached to hydrogen atoms indicate their direction of displacement at a particular phase of the ferroelectric mode of vibration.

hydrogens will jump, predominantly in a direction which enhances the local polarization set up by the ferroelectric mode. This will occur to an increasing extent as the instability is approached, since this is the point at which the potential wells become flat-bottomed. The antiferroelectric transition now appears as an instability against another mode which in $NH_4H_2PO_4$ happens to have a lower frequency than the ferroelectric mode, although the latter is also low. Inspection shows it to be a transverse mode with $\mathbf{q}=(0, 0, 2\pi/c)$; compare the last paragraph of § 3.

Few details of the structures of the phases of Rochelle Salt have yet been published, but the indications are that the transition cannot be described as a simple displacive one (Okaya *et al.* 1960). Nevertheless there is experimental evidence for the occurrence of a frequency $\omega_F/(2\pi) \sim 10^{10}$ c.p.s. in this crystal, and this frequency is lowest at the Curie points (Akao and Sasaki 1955). If we assume that results which have been derived using the harmonic approximation apply to KH_2PO_4 at least as a first approximation, then the corresponding frequency in this crystal can be estimated. From the fact that all involve the same (temperature-dependent) elements of the matrix $\mathbf{H}^{(0)}$ it can be deduced that the pattern of displacement of the atoms is the same in all of the following circumstances: (*a*) in the ferroelectric mode of vibration, (*b*) when a field is applied parallel to the ferroelectric axis and (*c*) when the crystal is sheared about this axis. It follows that the value of $\mathscr{P}_\gamma^2(F)/\sigma_F$ in eqn. (4.9) can be estimated from the spontaneous polarization and the measured displacements of the atoms in the polarized phase. Neglecting the contribution of modes other than $j=F$, eqn. (4.9) leads to

$$\omega_F^2 = \frac{P^2(T-T_c'')}{\mathscr{C}\rho\overline{u^2}}, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (5.1)$$

where P is the spontaneous polarization, $\mathscr{C}$ the Curie constant, ρ the density and $\overline{u^2}$ the weighted mean square displacement of the atoms, that is

$$\overline{u^2}\sum_K m_K = \sum_{K\alpha} m_K u_\alpha^2(K), \qquad . \quad . \quad . \quad . \quad . \quad . \quad (5.2)$$

where $\mathbf{u}(K)$ is an individual displacement. Experimental values are approximately $\mathscr{C}=260°$, $T-T_c''=175°$ at room temperature, $P=4\cdot 8\,\mu c/\text{cm}^2$ and $\rho=2\cdot 35$ g/cc. The oxygen tetrahedron is approximately undistorted after the transition, $u(\text{pot.})-u(\text{oxy.})=+0\cdot 04$ Å, $u(\text{phos.})-u(\text{oxy.})=-0\cdot 08$ Å parallel to the c-axis and $u(\text{hyd.})=0\cdot 2$ Å in a perpendicular direction (Bacon and Pease 1955). The estimated value of $\omega_F/(2\pi)$ is therefore $2\cdot 5\times 10^{12}$ c.p.s. or about 85 cm^{-1} at room temperature, decreasing to a minimum of about 14 cm^{-1} at the transition temperature. These cannot be expected to be correct in more than order of magnitude.

The first dispersion frequency of χ_3 is certainly higher than $2\cdot 5\times 10^{10}$ c.p.s. (work by W. A. Yager, quoted by Känzig 1957). Very recently the infra-red absorption in the range 500–100 cm^{-1} of solid potassium, rubidium, and ammonium dyhydrogen phosphates and of potassium dihydrogen arsenate has been studied by Hadzi (1961) who remarks that the group of ferroelectrics exhibits strong absorption, extending from above 500 cm^{-1} to below 200 cm^{-1}. In certain materials including KH_2PO_4 an absorption band was found at about 120 cm^{-1} and did not appear in the spectrum of the deuterated analogues, for which $T - T_c''$ is smaller. (This band has been attributed by Hadzi to direct transitions between the split zero level of the OH oscillator.) The temperature dependence and polarization of these bands do not appear to have been measured.

The Curie constants of ferroelectrics cover a wide range. In a crystal which is diagonally cubic, $\mathscr{C}$ is equal in order of magnitude to the inverse of the temperature coefficient β appearing in eqn. (3.14), irrespective of the number of atoms per unit cell. However this relation does not hold for crystals of lower symmetry. In crystals having about the same values of ω_F, eqn. (4.9) indicates that different values of $\mathscr{C}$ mainly reflect different values of the oscillator strengths $\mathscr{P}^2(F)/\sigma_F$, of their ferroelectric modes. It is therefore possible in principle for a crystal to make a transition of the displacive type discussed here without exhibiting any large anomaly in its dielectric properties, provided that the transverse optic mode with $q \rightarrow 0$ against which it becomes unstable is symmetric. A comparison of the structures of α and β quartz strongly suggests that the transition in this material provides an example.

Broadly similar conclusions on the order of magnitude and temperature dependence of the frequencies of vibration modes in ferroelectrics and in quartz have been reached by Ginzburg (1960) and by Ginzburg and Levanyuk (1960), whose treatment is essentially a phenomenological one.

ACKNOWLEDGMENTS

I am indebted to various colleagues for helpful comments on this work, particularly to R. A. Cowley. Some of the formulae quoted in § 3 were obtained in the course of work done jointly with Dr. F. A. Johnson, to whom I am also much indebted.

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ERRATUM

In Part I it was deduced that in the cubic perovskite structure there are, for values of q close to zero, three transverse optic and three longitudinal optic modes of vibration. There is in fact a fourth T.O. mode and a fourth L.O. mode, they have the same frequency and are symmetric. Having no polarization associated with them, they do not affect the dielectric properties of the crystal, and their omission from formulae given in Part I is correct, although their existence was in fact overlooked.

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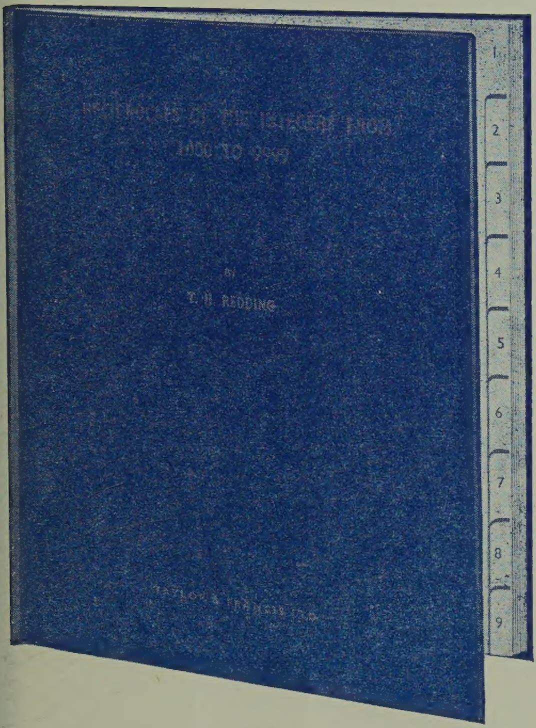

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In the first instance it was anticipated that an Appendix dealing with the advantages to be gained by the use of the reciprocal function in conjunction with such machines—and particularly with barrel-setting machines—would suffice to ensure the best use being made of the tables. The present 22-page *Appendix*, however, goes further than this, since the discussion of the tables is prefaced by a description of barrel-setting machines and their (simplest) method of operation in the evaluation of products, quotients and compound fractions. Thus, the description of each calculating procedure is followed by a numerical example with accompanying diagrams to illustrate the keyboard-displays at the beginning, the end, and at intermediate stages in the calculation. The machine-evaluation of series comprising the sum of a number of product or quotient-terms is also discussed. Generally it is hoped that the Appendix will serve as an introduction to mechanical methods of computation and that it will materially assist prospective purchasers in the choice of a machine.

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